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Trace Gas Analyzer Program

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FINAL REPORT

TRACE GAS ANALYZER (TGA) PROGRAM

Contract NAS9-14637

February 1977

Prepared for:

National Aeronautics and Space Administration
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Houston, Texas

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ABSTRACT

This report describes the design, fabrication, and test of a breadboard Trace Gas Analyzer (TGA). Capability to monitor Spacelab atmospheric contaminants in the atmosphere of the Spacelab provides flexibility in payload equipment selection. The effort was undertaken to verify that the required technology exists; much has been flight qualified.

The TGA is a gas chromatograph/mass spectrometer system, many elements of which were developed during the Viking Mars Lander program. The gas chromatograph subsystem employs a recirculating hydrogen carrier gas. The recirculation feature minimizes the requirement for transport and storage of large volumes of carrier gas during a mission. The silver-palladium hydrogen separator which permits the removal of the carrier gas and its reuse also decreases vacuum requirements for the mass spectrometer since the mass spectrometer vacuum system need handle only the very low sample pressure, not sample plus carrier.

Organic compounds are separated in a Witconol capillary column; carbon monoxide is separated from nitrogen in a molecular sieve column. The compounds separated by the gas chromatograph are identified and quantitated with a Viking mass spectrometer which scans over a mass range of 12 to 250.

System performance was evaluated with a representative group of compounds. The sensitivity was shown to be adequate.

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1.0 SUMMARY

An instrument is required to identify and measure concentration of low levels of toxic gases in the Spacelab atmosphere to ensure safety of crew members. A miniaturized breadboard Gas Chromatograph Mass Spectrometer was designed and built to meet this requirement. It is capable of identifying and measuring the concentrations of a wide variety of compounds at very low levels. The Trace Gas Analyzer (TGA) automatically injects a sample of the atmosphere into one of two gas chromatograph columns. The atmospheric constituents in the sample are separated in these columns and the effluent passes into the mass spectrometer for quantitative measurement and identification.

This breadboard system was built using residual flight-proven components from the Viking GCMS program. Testing demonstrated that a series of representative organic compounds can be detected well below toxic levels. These compounds included methylethyl ketone, ethyl acetate, methylene chloride, methanol, o-dichlorobenzene, and carbon monoxide.

The results obtained from the TGA breadboard provide a basis for proceeding with a program leading to the development of a Flight Trace Gas Analyzer.

1.1 Results

Engineering tests on the breadboard Trace Gas Analyzer system demonstrated that all functional and design requirements were met. Science testing showed that the minimum detectable concentrations were: methylethyl ketone 0.1 ppm, ethylacetate 0.1 ppm, o-dichlorobenzene 0.2 ppm, methylene chloride 0.5 ppm, methanol 2 ppm, carbon monoxide 5 ppm. These minimum detectable concentrations are all within specification. All these compounds gave a linear response with concentration up to 150 ppm. Butene elutes with air and is undetectable for this reason. Carbon tetrachloride and methyl chloroform appear to be fractionated on the catalytic surface of the separator. Butyraldehyde is also not

detected. It is converted to butyric acid in the hot inlet system. The GC peak width at 1/2 height is stable to within 2 seconds. Elution times are stable to ± 15 seconds. Operation of the breadboard TGA instrument in the fully automatic mode was demonstrated.

Testing of the TGA Breadboard demonstrated that the design approach will be appropriate for a flight system. The breadboard met its sensitivity and reproducibility specifications. All compounds tested give linear response over the concentration range of interest. The GC peak width and elution times have been demonstrated to be sufficiently stable for long-term, automatic GC operation.

Minor modification of the TGA Breadboard will permit measurement of chlorinated compounds. Butene will probably be detectable at the specified level when the effluent divider is operating in the 8000:1 mode. The required detection level for butene is 500 mg/m³.

Based on the TGA Breadboard test results, we conclude that a Flight TGA instrument can be built to meet all performance requirements within the Shuttle interface constraints. The flight instrument will be self-contained requiring only raw spacecraft power in and will yield a data stream output for transmission to the ground.

3.0 RECOMMENDATIONS

We recommend that development of a Flight Trace Gas Analyzer proceed by:

- Modification of the breadboard for the enhanced detection of chlorinated hydrocarbons at low concentrations.
- Development of a data system for TGA and testing this data system as part of the TGA Breadboard.
- Completely defining the interface requirements between the Shuttle and TGA.
- Incorporating improvements in the breadboard to optimize system performance.
- Continuing system testing with other compounds of interest.

4.0 INTRODUCTION

This is the Final Report for the Trace Gas Analyzer (TGA), Contract NAS9-14637. In this phase of the program, Beckman and Perkin-Elmer designed, fabricated, and tested a breadboard TGA.

The TGA instrument is designed for use on the Shuttle. The Shuttle missions are long duration; to protect crew health, it is absolutely essential to monitor concentrations of contaminants in the atmosphere. The TGA instrument has the capability to identify traces of individual contaminants at levels well below toxic concentrations. This implies a detection capability for organic and inorganic compounds in the range of parts per million, or even parts per hundred million. To do this under the constraints imposed on flight equipment, the instrument must be small, lightweight, use minimum power, and must be the most reliable analytical instrument available.

Under contract to NASA/JSC, Beckman and Perkin-Elmer have demonstrated the feasibility of performing these measurements with the TGA instrument. This instrument employs a GCMS (gas chromatograph-mass spectrometer). It permits the analysis at very low concentrations of virtually any organic compound. The system is capable of separating and identifying organic compounds that may occur whether expected or not. The TGA instrument is based on the GCMS system employed in the Viking Lander. The Viking system has already been qualified for a much more severe environment than is required of TGA. The Viking GCMS has functioned successfully on both Viking Landers on the surface of Mars, and has made critical analyses of the Martian soil. This instrument is the basis for the breadboard built by Beckman and Perkin-Elmer, the team that was also responsible for the Viking GCMS system.

One of the key TGA subsystems is the double-focusing mass spectrometer which has the same design as the Viking unit. This item of proven flight hardware meets all the system requirements for TGA.

Another key item of Viking equipment that was used on TGA is the hydrogen separator. The separator permits the reuse of hydrogen carrier gas and enables the TGA to employ a very low volume tank for hydrogen storage, thus minimizing overall system weight. In addition, a much smaller ion pump is required since the high efficiency separator allows very little carrier gas into the mass spectrometer.

A considerable design effort was required on Viking to develop very low leakage valves that operate at high temperatures. The Viking valves will operate up to 225°C with a leak rate of less than 10^{-8} std ml of helium per second. These valves were used on TGA.

Many other Viking parts are directly applicable to TGA, including small tubings and fittings. The thermal zone design and some column packaging techniques are also appropriate.

FIGURE 4-1 shows how the flight-qualified GCMS system is modified into the TGA breadboard which will then lead directly to a flight TGA system.

The first phase of the program was for the development of a breadboard model of the TGA. It was not intended to be a flight system, but the design of the system components is sufficiently close to that of a flyable version so that redesign will be minimized. Before describing the instrument built by Beckman and Perkin-Elmer, a brief description of the operation of a GCMS system is presented.

A GCMS system is one of the more powerful analytical tools developed in recent years. The major advantage of the system derives from the ability of the GC to separate compounds when they occur in a complex mixture, and from the capability of the MS to identify (or to provide data for the identification) and provide a quantitative measurement of the individual compounds in the atmosphere. As shown in FIGURE 4-2, a sample of the atmosphere to be analyzed is injected into the GC; carrier gas flowing through the column causes the different compounds to move through the column at different rates which are dependent on their interaction with the stationary phase of the column. The

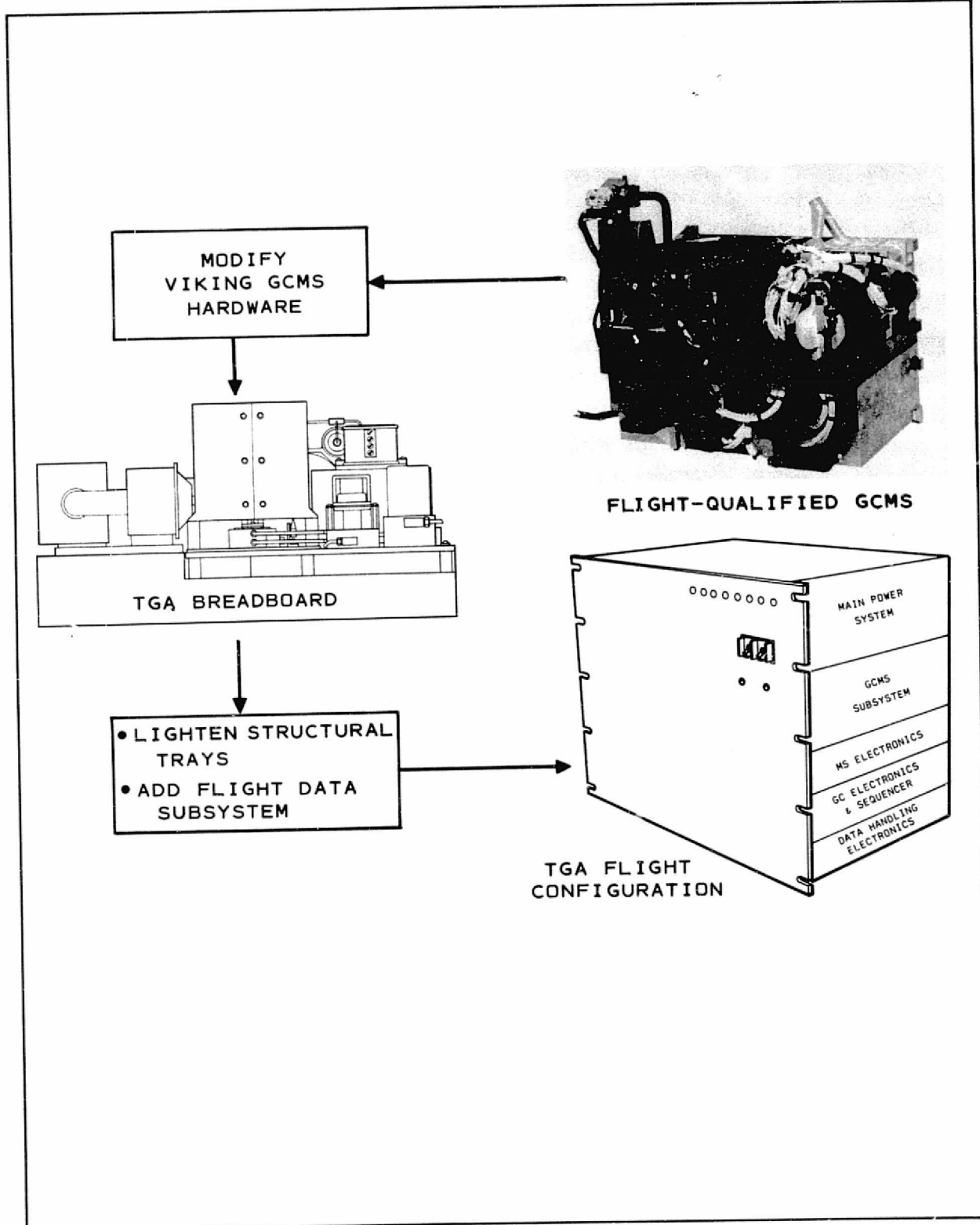


Figure 4-1. Development of TGA Flight Instrument

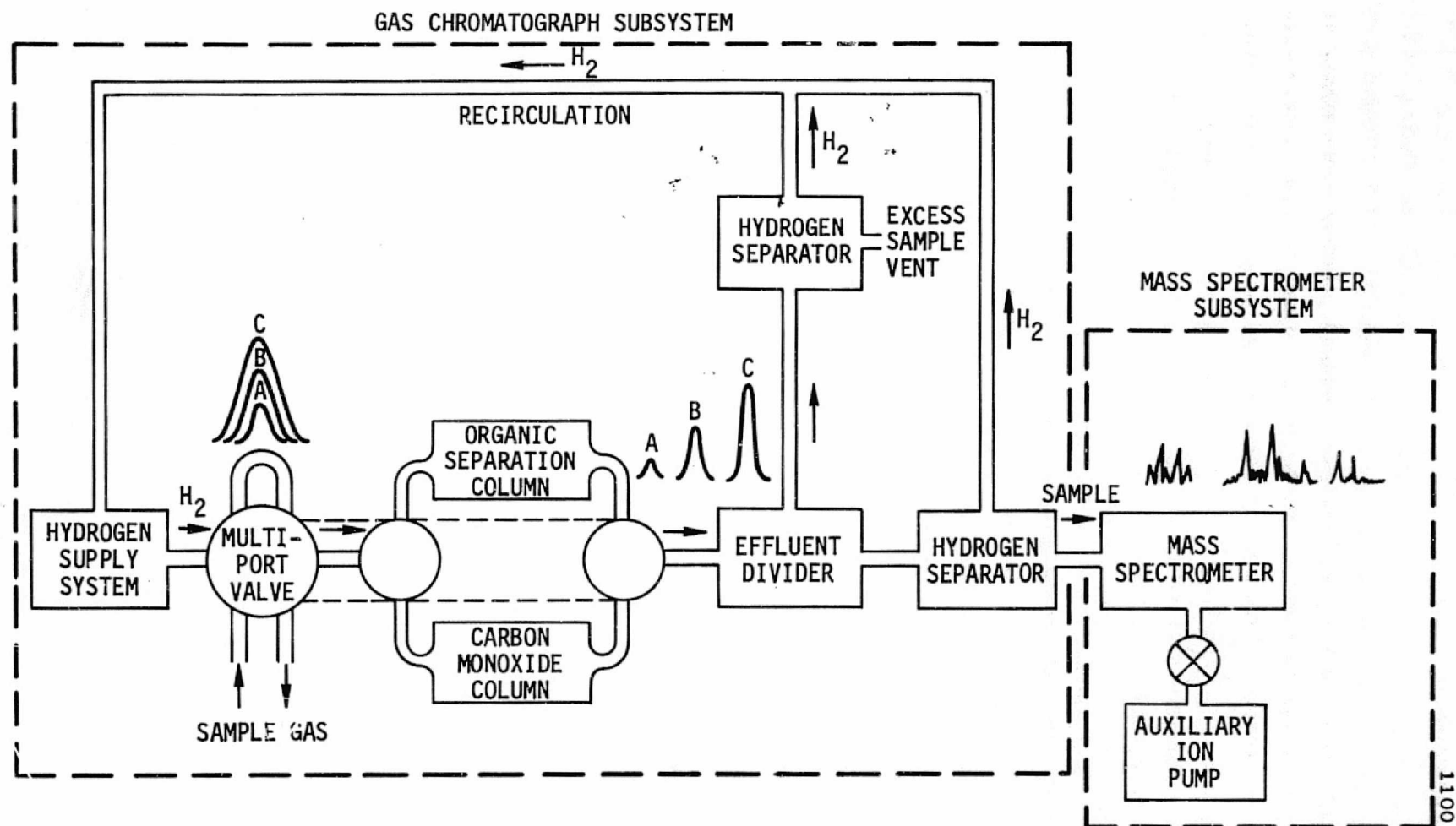


Figure 4-2. System Gas Flow Diagram

separated components elute from the column and pass through a separator where all of the carrier gas is removed prior to entry into the mass spectrometer. In the mass spectrometer, the compounds are ionized and separated by their mass-to-charge ratios. The mass spectra serve as a means of identifying the compound; the intensity of the spectra is dependent on the partial pressure of the compound in the source.

The compounds of interest are primarily low-molecular-weight, organic compounds--such as cleaning agents, volatile metabolic products, monomers of some plastics, and certain toxic gases. The detectable levels for the components by the TGA must be lower by some significant amount than the "maximum allowable concentration." The detectable limits are generally in the range of 0.5 to 200 ppm.

Automatic operation of the TGA breadboard is controlled by an electronic sequencer. An analysis cycle time of 2 hours was achieved.

5.0 BREADBOARD SYSTEM DESCRIPTION

5.1 Design Approach

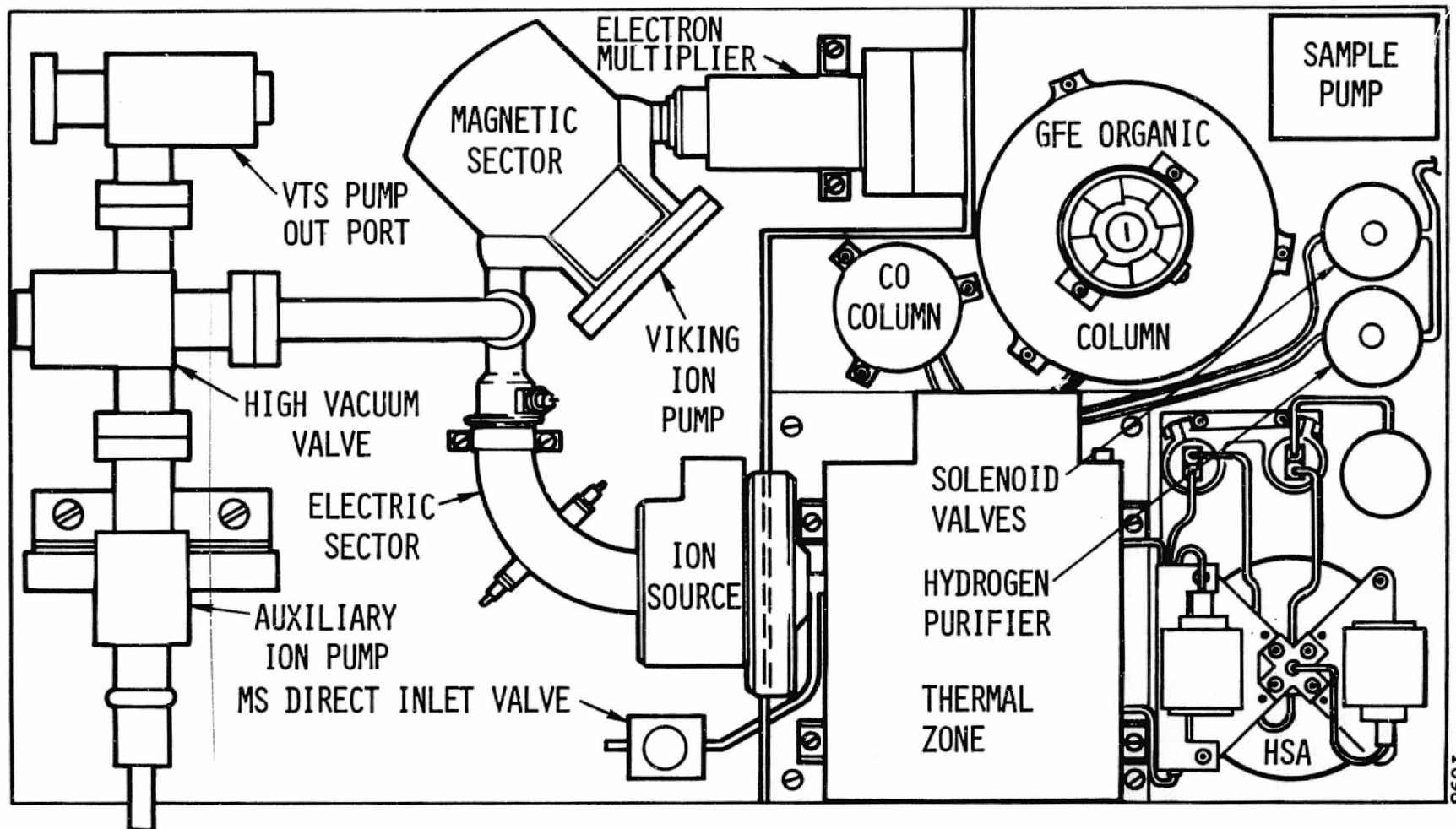
Some Viking GCMS residual components were used to build the TGA breadboard. This approach allowed major components to be assembled in a flight-type configuration, while retaining the accessibility for the ease of change required of the breadboard model (FIGURE 5-1). The system has been conceived so that well defined interfaces exist between all subsystem components.

The breadboard consists of three major subsystems: gas chromatograph (GC), mass spectrometer (MS), and electronics (FIGURE 5-2). Viking GCMS experience has demonstrated the desirability of packaging the GC and MS subsystems independently, with separation at the subsystem level. This allows each complete subsystem to be fully tested before integration and permits MS or GC removal, if servicing is later required.

The breadboard electronics were packaged primarily in external equipment racks, using hard-wired Vector board techniques where possible. Viking flight-qualified circuit designs were used where applicable, minimizing circuit design and development time. Critical MS electronics were mounted on the MS subsystem tray. The TGA breadboard was mounted on a Viking Vacuum Test Station (GFE) during system testing.

5.2 System Operation

Samples of the atmosphere are drawn into sample loops with a sample pump just before the start of an analysis (FIGURE 5-2). The sample valve takes a precisely-measured volume of the gas (about 0.5 ml) and introduces it into either a column which separates the organic compounds or into another column which separates carbon monoxide from nitrogen. Organic and carbon monoxide analyses are performed sequentially.



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Figure 5-1. TGA Breadboard Sensor Tray

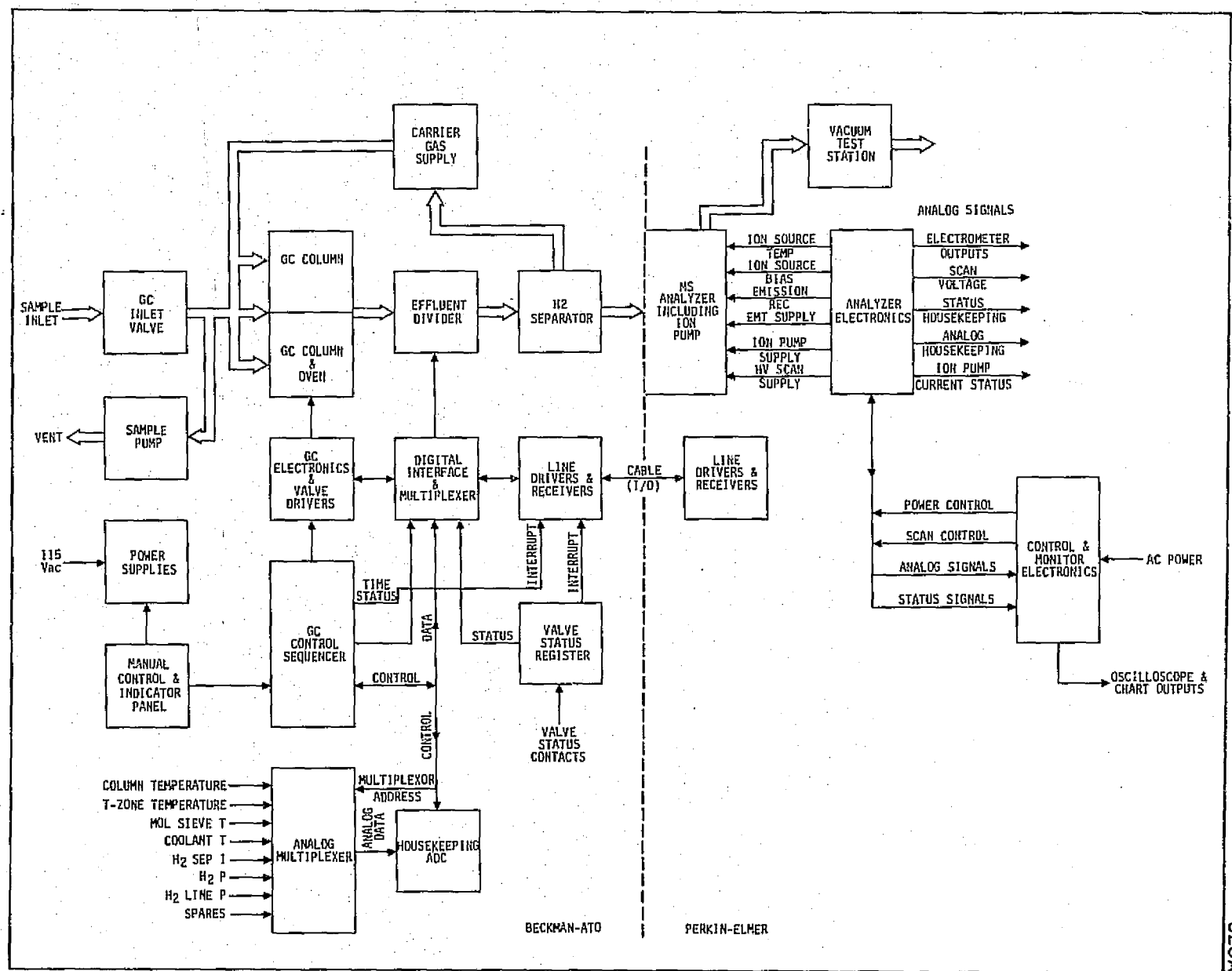


Figure 5-2. TGA Breadboard System Block Diagram

The effluent from either column flows through a divider and then into a hydrogen separator. The hydrogen is separated from the sample and is returned to the carrier gas supply system. The function of the effluent divider is to extend the dynamic range of the instrument and to protect the MS from large sample overloads. The gas exiting the separator is comprised of the sample components from the atmosphere, undiluted by carrier hydrogen.

Precise control of analytical conditions (flows, temperature, timing, etc.) is required to control the elution time of each sample component. Because the elution time is held relatively constant, component identification by the MS is greatly simplified.

The entire system can be operated in either the manual mode or under the control of an automatic sequencer. The data output includes housekeeping data as well as data from the MS. The mass spectral data are recorded on an analog recorder. The breadboard system has provisions for displaying data on an oscilloscope, or recording on an oscillograph.

5.3 Mechanical Configuration of the Breadboard System

The GC and MS subsystems were packaged on independent tray assemblies requiring only one flow system interface connection. Other interfaces were structural only, and were designed for easy separation.

A simple GC subsystem tray was fabricated to support the GC subassemblies. This tray was attached to a plate to which the MS had previously been connected.

The GC and MS subsystem interface is very similar to the Viking design. Since the MS inlet system must be kept warm, the MS inlet valve mounts in the GC Thermal Zone subassembly. Accordingly, the MS Ion Source and GC Thermal Zone are mounted at the corresponding edges of their respective trays. Thermal Zone and the GC subsystem tray designs allow easy access and provide the required mechanical orientation between the respective subsystem components.

This mechanical packaging concept made maximum use of Viking hardware and leads directly to a flight qualified design. Individual subassemblies were as small as practical, yet allowed sufficient access for breadboard testing.

5.4 TGA Breadboard Assembly

After assembly and checkout of the major subsystem (GCS and MSS), these units were integrated by sliding the two trays together and attaching the fitting associated with valve V7. Valve V7 is the valve that controls the inlet from the GCS to the mass spectrometer. V7 is mounted in a saddle located in the thermal zone. The valve wires and cable interface between the mass spectrometer GCS and the supporting electronics are connected.

For the breadboard, the organic column (GFE) is mounted in an external oven. It is connected to the breadboard by 0.51-mm (0.02-inch) ID stainless-steel lines. These lines are heated by resistance wire which is wrapped around them. The line temperatures are controlled and monitored. The complete breadboard assembly of the mass spectrometer and the GCS is shown in FIGURE 5-3.

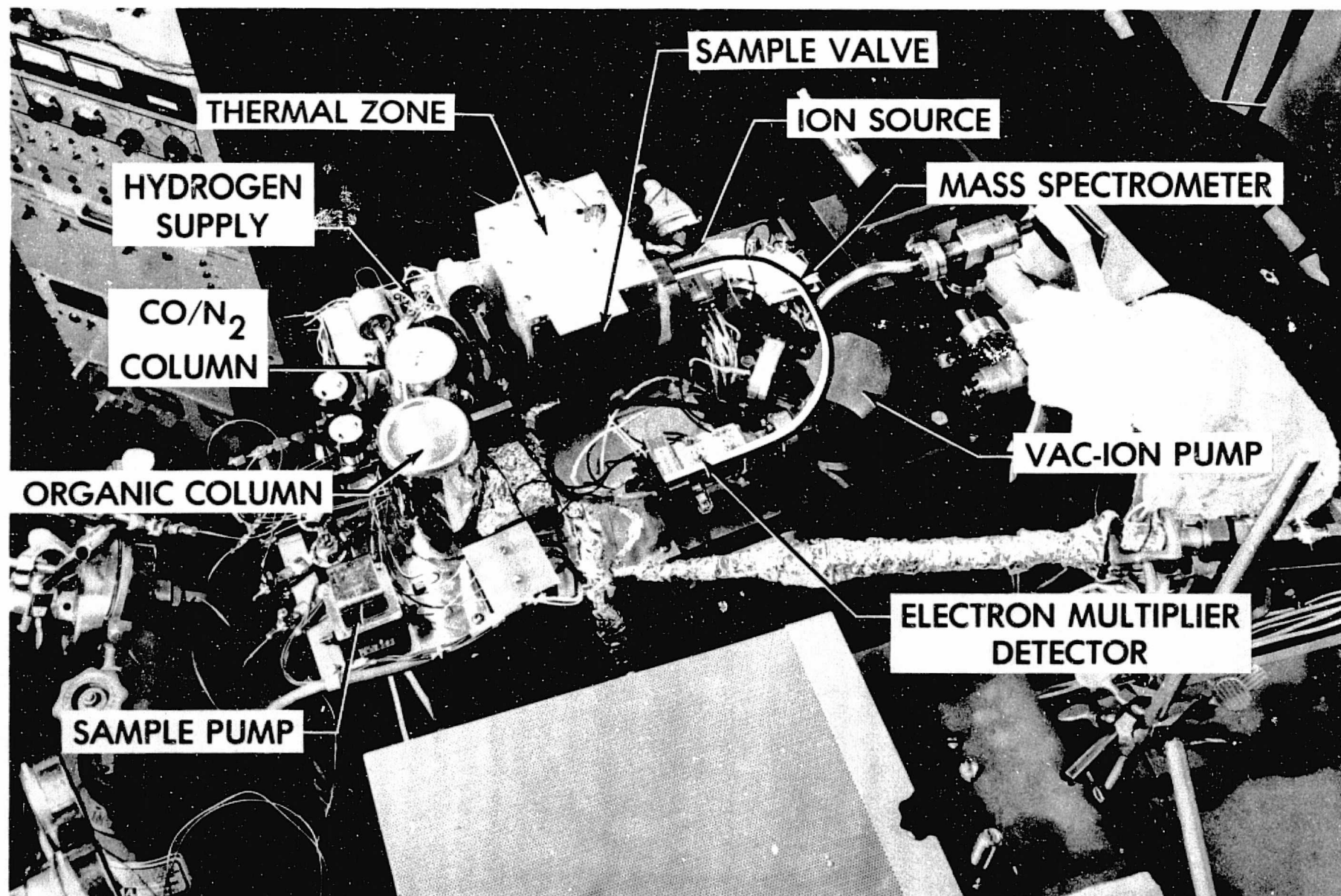


Figure 5-3. TGA Breadboard Assembly

6.0 BREADBOARD GAS CHROMATOGRAPH SUBSYSTEM (GCS)

6.1 Introduction

The GC subsystem supplies carrier gas to carry the sample components through the column and into the MS. The gas flow diagram for the GC assembly is shown in FIGURE 6-1. The GCS consists of four major subassemblies:

- Carrier gas supply--supplies constant flow of hydrogen.
- GC Columns--these columns separate the sample components.
- Thermal Zone--this maintains the effluent divider, sample valve and hydrogen separators at elevated temperatures.
- GC Electronics--this contains the power supplies and control circuits to support the GC subsystem.

Each major subassembly was assembled and tested before integration into the GC subsystem. The subassemblies were checked for leaks, contamination, and performance before they were assembled onto the tray. After assembly, they were again leak-checked. After assembly with the mass spectrometer, the single interconnecting fitting was also leak-checked.

The following sections give details of certain techniques used for component construction or subassembly fabrication. Although procedures similar to those used on Viking are not discussed at length, procedures that are unique to the TGA breadboard are discussed in detail.

After mechanical assembly, each subassembly in the GCS was helium leak-checked and electrically tested to ensure that all components were sealed together and were functioning properly. The units were then performance-checked or tested where possible to avoid potential problems after final assembly of the complete TGA breadboard system.

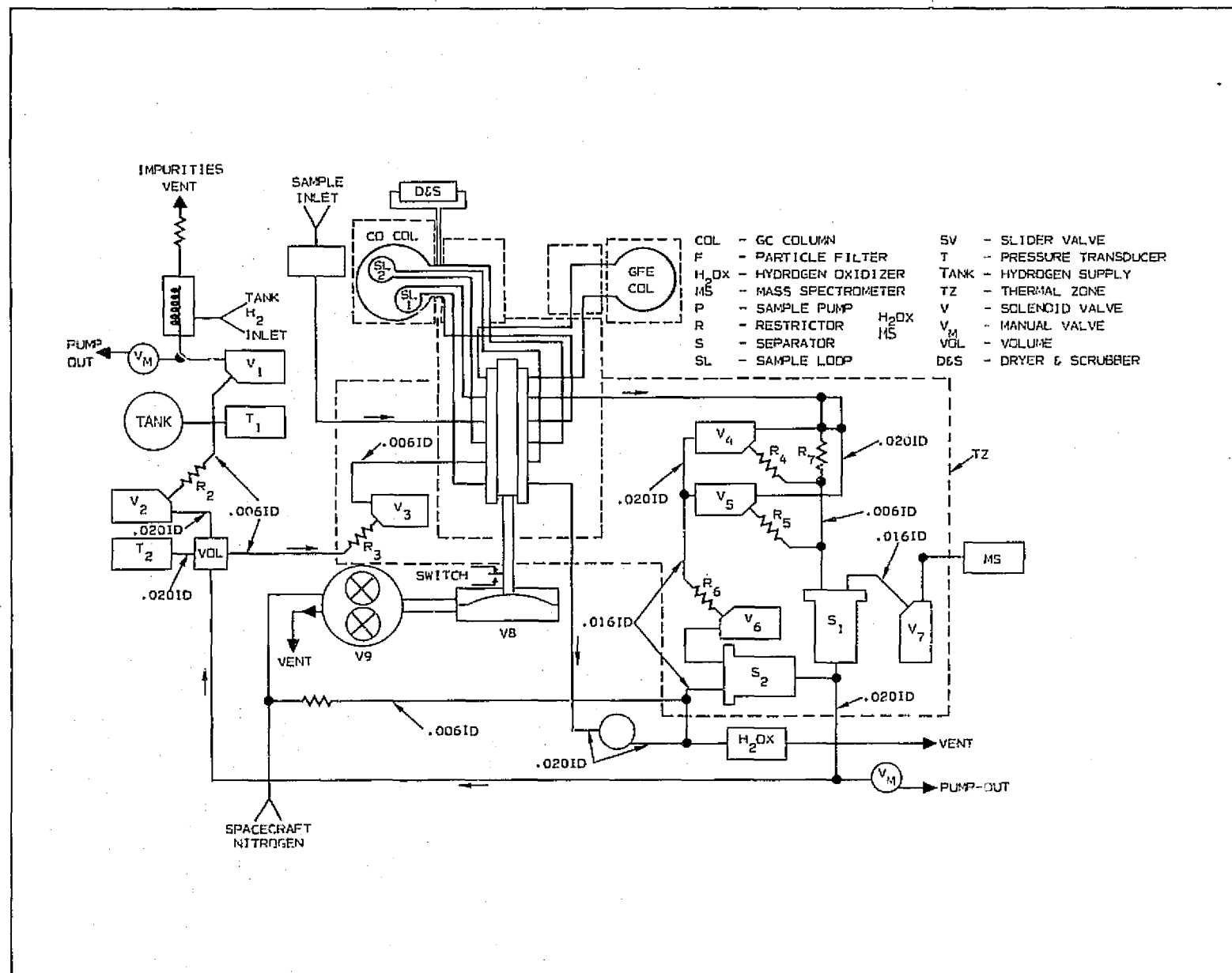


Figure 6-1. GC Assembly Gas Flow Diagram

6.2 Carrier Gas Supply and Flow Control

The carrier supply assembly provides hydrogen at a constant flow rate to transport the sample components through the GC column to the MS for identification and quantitation. The carrier supply assembly consists of three major components:

- Hydrogen Purifier
- Storage Tank with Pressure Monitoring Transducer
- Flow Control System

The gas flow diagram for the Hydrogen Supply Assembly is shown in FIGURE 6-2.

6.2.1 Hydrogen Purifier

The hydrogen purifier assures the quality of the hydrogen carrier gas. This is accomplished by passing the hydrogen through heated silver palladium tubing as the hydrogen supply assembly is filled. The purifier is attached upstream of the hydrogen supply assembly (FIGURE 6-3). It consists of a silver palladium tube mounted in a stainless-steel tube. One end of the silver palladium tube is sealed and the other is attached to the hydrogen supply assembly through valve V1. The breadboard purifier is heated with a cartridge heater driven by a Variac. A temperature controller will be required in the ground support equipment for a flight unit of the TGA.

Impurities in the carrier gas must be small (less than 0.1 ppm) so they do not interfere with sample measurement. These levels were easily obtained on the Viking GCMS carrier gas supply by using a silver palladium purifier to purify the hydrogen when the tank is filled. For the TGA system, before filling, the tank, connecting lines, and purifier were vacuum-baked for several days to pump out any impurities. The clean system remains intact so that refilling of the tank after a mission or test requires no bake-out or evacuation.

6.2.2 Storage Tank

Under conditions of continuous analysis for 60 days, and at a flow rate of 4 ml/min, the total hydrogen that flows through the system is 346 liters. To

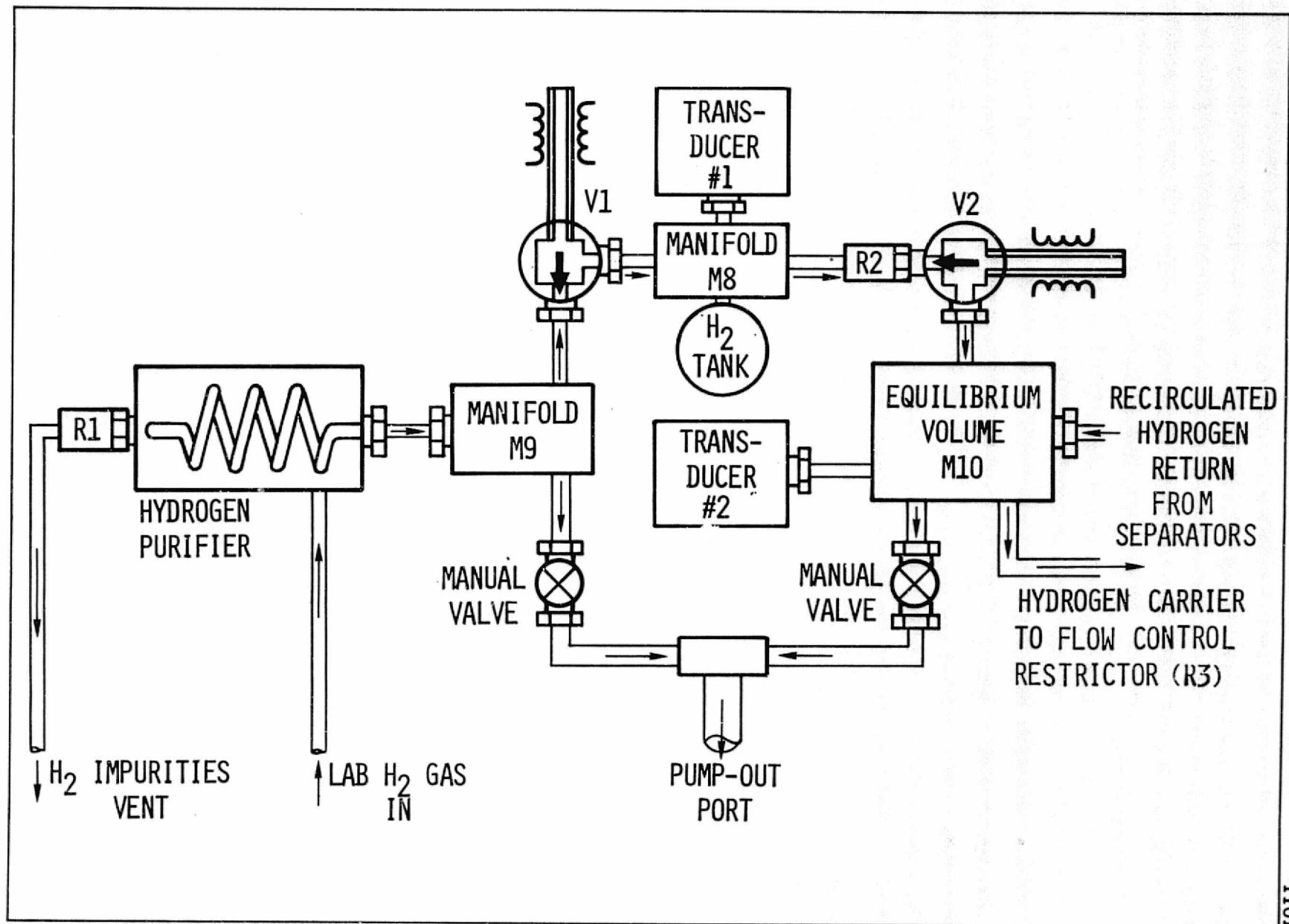


Figure 6-2. Flow Control System

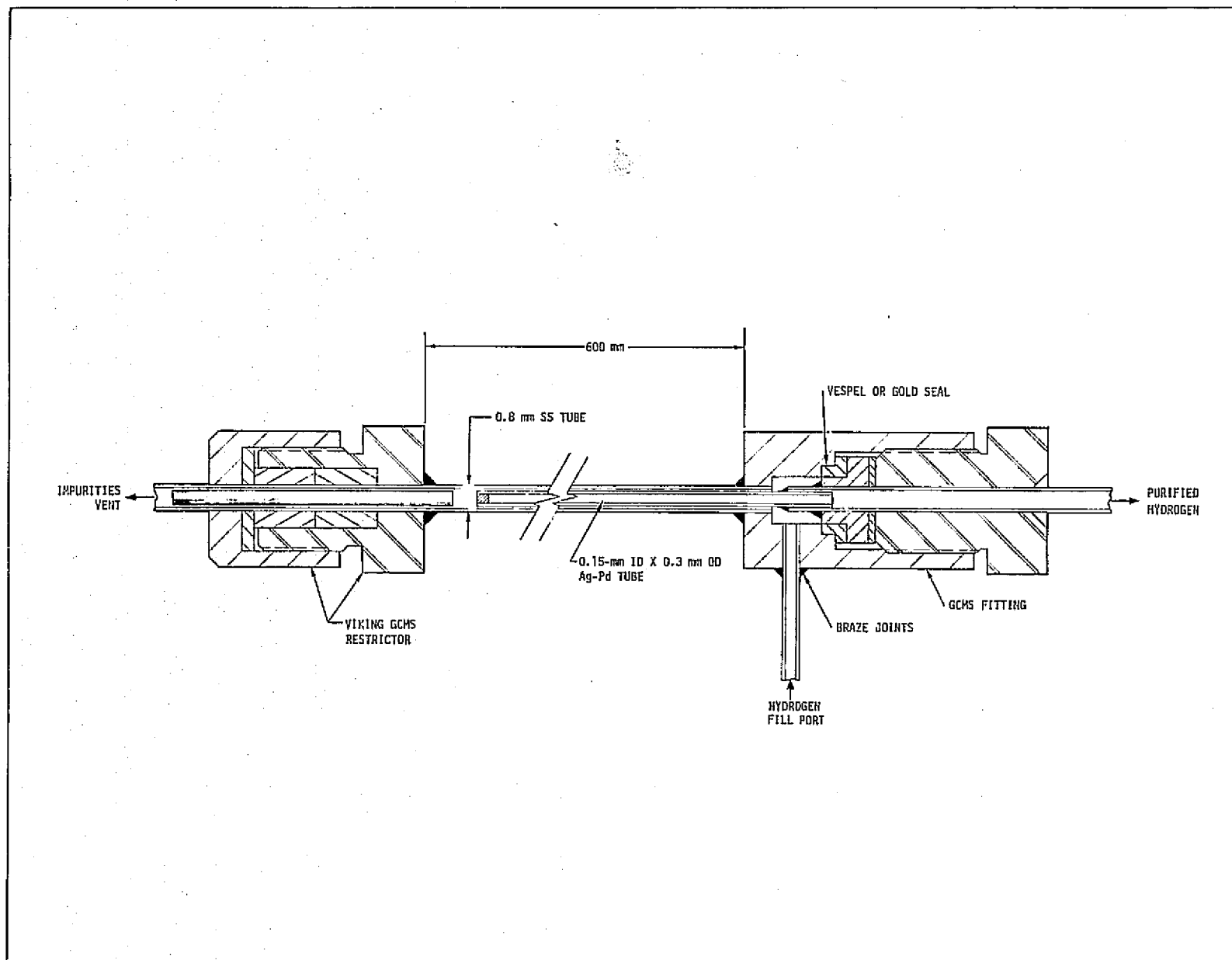


Figure 6-3. Hydrogen Purifier Before Packaging

contain this volume of gas would require a large tank. However, if the carrier gas is recirculated the gas storage capacity requirement is decreased. The same tank and pressure transducer that were developed for the Viking GCMS was used on the TGA breadboard. This unit and its mounting hardware have been fully tested and flight qualified.

The tank will contain 12.8 liters of hydrogen when pressurized to 6.9 MPa (1000 psig). The tanks used on Viking are all proof-tested at 10.3 MPa (1500 psig). Gas losses in the recirculation system will occur only when the sampling valve is switched. For a one-ml sample-loop volume (maximum) at about three atmospheres of pressure, and for two analyses per hour (maximum), the gas loss is 6 ml/hr, or 144 ml/day. This quantity of hydrogen gas can be vented safely through an Ag-Pd oxidizer to the Shuttle cabin atmosphere. The useful operating pressure range of the tank is between 1.72 and 6.9 MPa (250 and 1000 psig) so that 9.6 liters of carrier gas are available. Therefore, there would be sufficient hydrogen to continuously sample for 66 days (twice the maximum mission length).

The hydrogen storage tank assembly includes a pressure transducer that reports to the instrument data system the pressure remaining in the hydrogen tank. This pressure transducer was qualified on the Viking program.

6.2.3 Flow Control System

These components are assembled as shown in FIGURE 6-2. The system operates in the following manner:

- Valve V2 is opened until the pressure in the "interconnecting volume" reaches a preset level.
- V2 is then closed by the automatic pressure control circuit.
- Valve V3 is then opened to allow flow to the system.

Valve V2 cycles to hold the pressure in the damping volume constant until system equilibrium is reached, at which time the recycled hydrogen replenishes the hydrogen lost through R3, so V2 remains closed. The only time hydrogen needs to be added to the semi-closed system is immediately following a sample valve

actuation. Valve V2 only cycles until the system has re-equilibrated. The accurate pressure control, less than 34.5-kPa (5-psi) variation, is required to hold the flow through the system constant. With constant flow, the elution time of the sample components will remain in the same time-slot, which makes their identification easier. The estimated upstream pressure is 1.38 to 1.72 MPa (200 to 250 psig), which holds the flow constant to within 2%. If greater flow stability is required, the operating pressure is increased or the limits of the controlled pressure are tightened.

Instability in flow can be caused by variations of pressure in the sampling volume and the temperature of the flow control restrictor, R3. Pressure changes may be the result of transducer hysteresis and temperature changes of the transducer. The transducers used on Viking GCMS and used in this program show very little hysteresis (1% maximum) and are temperature compensated. The volume between R2 and V2 was minimized (0.15-mm ID tubing), so little pressure surge will occur in the damping volume when valve V2 is opened.

The hydrogen tank was filled using the previously described hydrogen purifier (FIGURE 6-3). Just downstream of the purifier is a three-tubed manifold. The third tube is attached to an MS for initial pumpdown, leak check, and contamination measurement. When the tank and associated hardware (valves, volume, restrictors) are free of impurities, this pumpout tube is sealed (pinched off for a flight system). This "pinch-off" sealing procedure was thoroughly studied and was used on the Viking GCMS to seal the hydrogen tank after filling. The breadboard unit has a manually operated valve to seal the pumpout port.

Pressure control to the required accuracy (± 1.72 kPa or ± 2.5 psi) was obtained with this system, which results in accurate (± 15 s) elution of the sample components.

The carrier gas supply system is constructed from flight-type hardware (except feedback circuit), so the conversion from a breadboard instrument to a flight instrument will require minimum redesign. The feedback circuit for accurate pressure control was thoroughly tested during component development testing.

Two high-pressure restrictors are used in the flow control system. These are R2 and R3. The restrictors are set under dynamic flow conditions. They are temperature-cycled and pressure-pulsed by opening and closing an adjoining valve to ensure stability of their restriction value. The two restrictors are set under slightly different conditions.

Restrictor R2 (FIGURE 6-1) is set for 2.5 std ml/min flow at 1.72 MPa (250 psi) pressure and ambient temperature. All restriction adjustments are made at 125°C, and the restrictor is temperature-cycled from ambient to 125°C to stabilize it.

Restrictor R3 (FIGURE 6-1) is located in the thermal zone; therefore, it was held at 220°C during breadboard system operation. To set this restrictor, it was assembled and then heated to 220°C. A preliminary restriction adjustment was made to 6 std ml/min at 1.38 MPa (200 psi) head pressure. After several valve cycles and temperature cycles, the restriction was adjusted to 4.5 std ml/min. After more valve cycles and another temperature cycle, the restriction was finally set at 4 std ml/min on the low side of the pressure range. There were several more valve cycles and another temperature cycle. The setting was checked and the final adjustment was made to set the restrictor to 4 std ml/min at 220°C and 1.34 MPa (195 psig). At this point R3 was ready for installation in the thermal zone.

6.2.4 Construction and Test of the Carrier Gas Supply Assembly

All components of the carrier gas supply assembly were cleaned with Freon TF and then assembled. All GCMS-type fittings were torqued to the optimum value 2.26 to 2.49 N·m (20 to 22 inch-pounds). The unit was leak-checked using helium leak detector. No detectable leak was permitted. A very small amount of diffusion can be seen but can be distinguished from a leak by the rate at which the leak detector signal increases. After the HSA is assembled, it is leak-checked in two ways. First, it is leak-checked by evacuating the inside of the tank while helium floods the outside of the tank. Under these conditions the leak rate should be minimal; that is, less than 1×10^{-11} std ml/s.

It is next leak-checked by placing it in a vacuum enclosure that is attached to a leak detector. The tank is pressurized to 10.3 MPa (1500 psi) with helium. The leak rate coming out of the tank is then noted and should be less than 1×10^{-10} std ml per second.

The pressure transducers are calibrated by filling the tank through the pumpout lines with ultrapure hydrogen or helium.

After the assembly has been satisfactorily leak-checked, it is attached to an ion pump vacuum station, evacuated, and heated to 125°C until the pressure reaches a stable level. Leaks and contamination are checked by closing the pumpout valve for a period of time after opening and watching the ion pump pressure. Several times during the early part of the pumpdown, hydrogen is flowed into the upstream side of the purifier to convert the palladium oxide to palladium and water. After cooling the connecting lines, the unit is isolated with the pumpout valves and then cooled to ambient temperature. The hydrogen cylinder is attached to the purifier and the hydrogen tank is pressurized to about 6.89 MPa (1000 psi). The HSA can then be stored waiting assembly into the GCS.

6.3 Column Assembly

The column designed to separate organic compounds was supplied as GFE and was not packaged for the breadboard system.

This column separates the organic compounds of interest, but does not separate CO from N₂ as required for MS detection of CO. For this separation we used a second column packed with Molecular Sieve 5A. This column packing material is widely used for separation of atmospheric gases. The elution time for heavier materials is very long on this column.

The gas flow rates through these two columns must be very nearly the same (about 4 std ml/min of hydrogen).

6.3.1 Organic Column

The organic column was supplied as a loose coil of tubing. It was used on the breadboard "as is" by using an air-circulating oven for isothermal and temperature programmed operation. For the flight unit, we propose to package the organic column and CO column into assemblies using the design developed for the Viking unit. This design is reliable and desirable for flight application.

Because the ambient temperature is not controlled accurately, the column temperature is controlled at a starting temperature of 60°C to ensure repeatability from one analysis to another. This permits accurate control of elution time of the sample components. Operation above ambient temperature is also required to allow the organic column to be cooled to minimum operating temperature in a relatively short period of time (<30 minutes).

Before the organic column was integrated into the breadboard, it was tested to check its compatibility with the hydrogen separator. The column was baked overnight at 120°C with 4 std ml/min of hydrogen flow. It was then attached to a separator and a Finnigan Model 750 Mass Spectrometer for measurement of transmitted hydrogen. After several overnight bake-outs at 120°C and several temperature cycles, the separator was still operating normally. From these test results, we conclude that the organic column and the hydrogen separator are compatible under the present operating conditions. These subassembly tests have been borne out by our ability to operate the organic column for long periods of time with no noticeable degradation of the separator.

6.3.2 CO Column

The CO column is used only to separate carbon monoxide from other gases, mainly nitrogen.

Carbon monoxide must be separated from nitrogen because the MS sees both at m/e 28; the large concentration of N₂ would mask the CO response and overload the MS ion pump. The CO column is sized to be compatible with the 4 ml/min flow rate of the hydrogen carrier gas. The column is packed with 60-80 mesh Molecular Sieve 5A (Linde) in a 0.76-mm (0.030-inch) ID tube 3.5-m (11.5 feet)

long. The pressure drop across the column was found to be 207 kPa (30 psi) for 4 std ml of hydrogen per minute.

The temperature of the column is held constant so the elution time remains constant (20 to 25 minutes). This column is heated to about 60°C, which is just greater than maximum ambient temperature.

The packed column is loosely coiled and is run through a preliminary check before it is wrapped on its mandrel and retested.

It is necessary to deactivate the Molecular Sieve column to prevent excessive tailing of the CO peak. This is accomplished by injecting several microliter volumes of water into the column while the column is held at about 120°C. This partially deactivates the column and decreases the tail on the CO peak. After several minutes the column is cooled to 60°C and is ready for installation in the GCS. Baking the column above 125°C reactivates the column and it must be again deactivated with water.

Interference from materials such as H₂O, CO₂, and organic compounds may occur after many samples because the column is not backflushed after each analysis. It may be necessary to pretrap the H₂O and CO₂ with a material such as LiOH. When breakthrough occurs, the MS signal will appear as if there were an increase in column background rather than as an eluted peak. At this time the column must either be baked out at an elevated temperature or must be replaced. A flight unit would probably be baked out during refurbishment between missions. If a pretrap is used, it will be sized to last for one mission, and will be readily replaceable during refurbishment.

6.4 Thermal Zone

6.4.1 Introduction

The GC thermal zone consists of the following components:

- Effluent divider
- Slider valve

- Restrictors
- Hydrogen separators

The breadboard thermal zone subsystem is made from some available miniaturized Viking components. The other components were constructed for the breadboard.

The gas flowing through the thermal zone must pass through a large number of valves, restrictors, and sections of tubing. It is important to minimize dead volumes since the carrier gas flow rates are very low. This is important so that the system will respond quickly to changes in sample concentration. The available Viking components were designed to function properly at low flow rates.

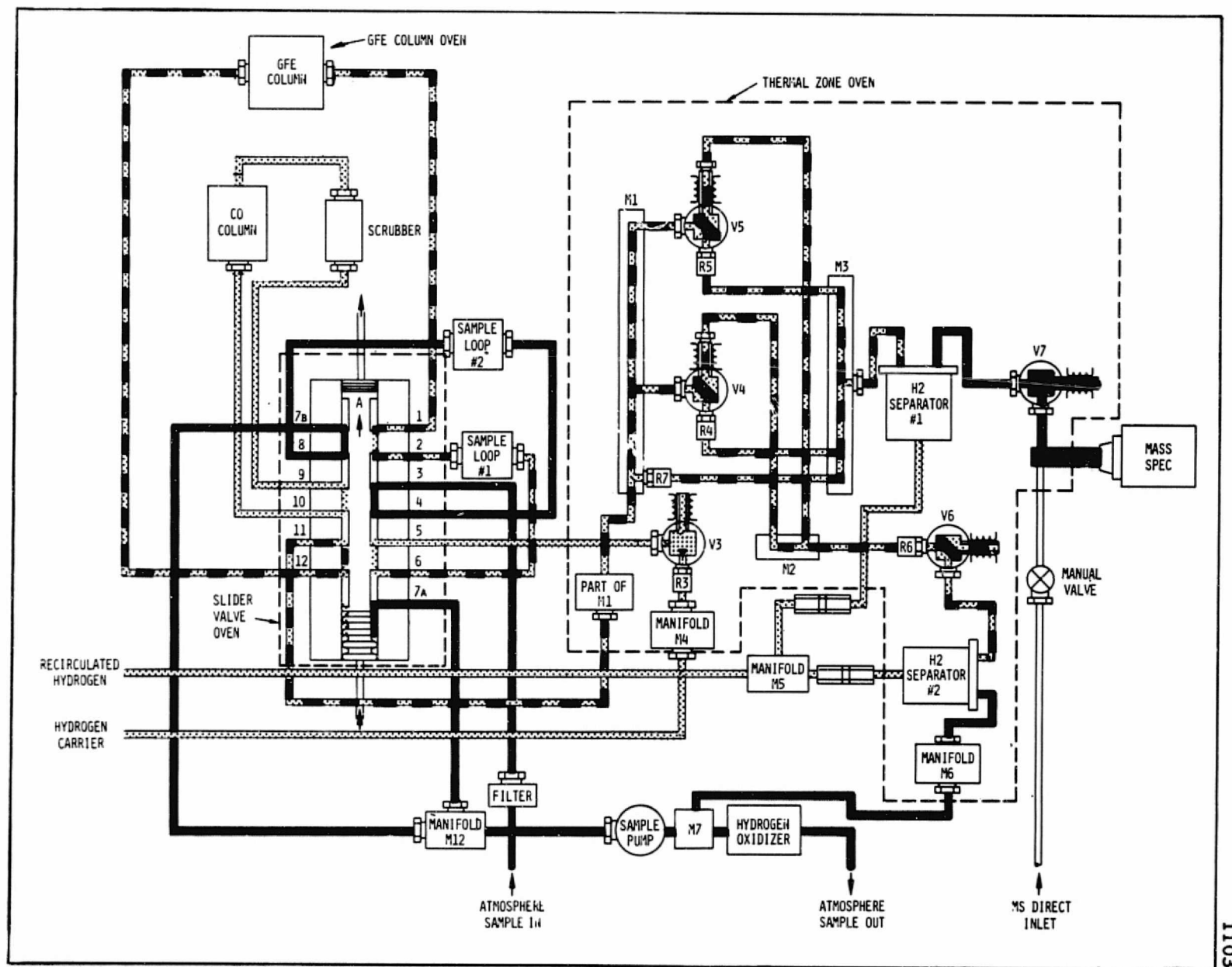
In general, the thermal zone contains all the components that must be located in a temperature controlled environment. The thermal zone was operated at 220°C during the course of breadboard testing. Initially the temperature of the thermal zone was set for 205°C but was increased to 220°C to increase the permeability of the separator for hydrogen. The thermal zone has in it a sample valve that is controlled at 170°C by a separate temperature controller.

As the thermal zone components were assembled, the fittings were leak-checked. The effluent divider was assembled and leak-checked on a separate fixture.

The effluent divider split ratios were checked at the T-zone level of assembly, using a hydrogen source and a Finnigan Model 750 Laboratory Mass Spectrometer. The separator efficiency was also checked at this stage of assembly. The breadboard thermal zone contains the items enclosed in the dashed lines in FIGURES 6-4 and 6-5. These figures show the gas flow through the sample valve and the thermal zone. FIGURE 6-4 shows the sample valve in the position to perform a carbon monoxide analysis; FIGURE 6-5 shows the sample valve in the position to perform an organic analysis.

6.4.2 Sample Valve and Actuator

The sample (slider) valve assembly is required to inject known volumes of atmospheric sample into the GCMS system for analysis. By switching the sample valve,



a constant volume of sample gas is injected into either the organic column for organic analysis or into a CO column for carbon monoxide determination.

The sample valve must meet the following requirements. The techniques used to meet each requirement are given:

- The sample valve must be leak-tight to ensure that no sample is lost and no air leaks into the system. This is accomplished by bolting the flanges together using coil springs to ensure sealing during temperature variations.
- The valve must be chemically inert since it cannot cause any changes in chemical structure of the sample or any sample absorption or desorption. The valve is made of chemically inert materials, such as stainless steel, and uses Vespel sliders.
- The valve must have low dead volumes to minimize GC peak broadening and peak tailing. This is accomplished with small grooves in the Vespel sliders and holes through the slider valve which are very small (0.51 mm or 0.020-inch dia).
- The position of the valve must be known so that the system status will be known. The sample valve actuation also initiates a clock timer and a signal must be available for this purpose. A status switch is located external to the valve and can be easily mounted because of the open mechanical structure of the valve.
- The valve operating temperature must be at least 10° greater than the maximum column temperature to prevent condensation and peak broadening. The slider valve is mounted to the thermal zone frame and its temperature is held at about 170°C.
- The valve must provide for injection of a constant sample volume of sufficient size to meet the detectability requirements. The sample loops are made of lengths of tubing each having an internal volume of 0.5 ml at 60°C. This volume is constant because the loops are located in a thermal zone at constant temperature and because the cabin pressure is anticipated to be controlled within 2%. If it is

necessary to change the sample loop volume, it can be easily done by changing the length of the tubing.

- The sample valve design should eliminate any long-term development effort. The design which was built for the breadboard is a miniaturized version of a proven valve design which has been used for many years in process chromatography. With only minor modification, the breadboard sample design can be converted to flight hardware.

The sample valve used in the TGA breadboard is shown in FIGURE 6-6. It is a pneumatically-operated valve. The pneumatic actuator is driven by a solenoid valve. An electrical solenoid or motor actuator will be used on the flight unit. The valve consists of two flanges that clamp on movable Vespel slides. The Vespel is in the form of poppets which are polished and then checked for any tendency to scratch a polished surface of 316 stainless steel. The holes through which the tubing enters the valve plates have a conical inset. The metal surfaces are coated with Dextsil 300. Originally, the valve was constructed from 316 stainless steel. This proved to be too soft and scratched too readily. The scratches caused gas leaks through the valve. Therefore, we went to a hardenable stainless steel, 440C, which was hardened to greater than Rockwell C50.

The valve is tested by heating it to operating temperature (160° to 170°C) and then actuating it. The position switch is checked to assure that it is functioning properly. Each poppet is leak-checked by attaching an appropriate line to the mass spectrometer and monitoring the argon peak. An argon gas purge is used to measure the leak rate and a nitrogen purge is used to determine system background at mass 40. The diffusion of argon through the poppets is determined by the rate at which mass 40 signal increases or decreases. The leak rate from each tube should be less than 1×10^{-8} std ml of argon per second. The measured leak rate at temperature for most of the poppets in the final design was 3.6×10^{-9} std ml of argon per second.

The initial design used a Teflon film over metal poppets. This showed a minimum leak rate due to diffusion at operating temperature of 1×10^{-7} std ml of argon

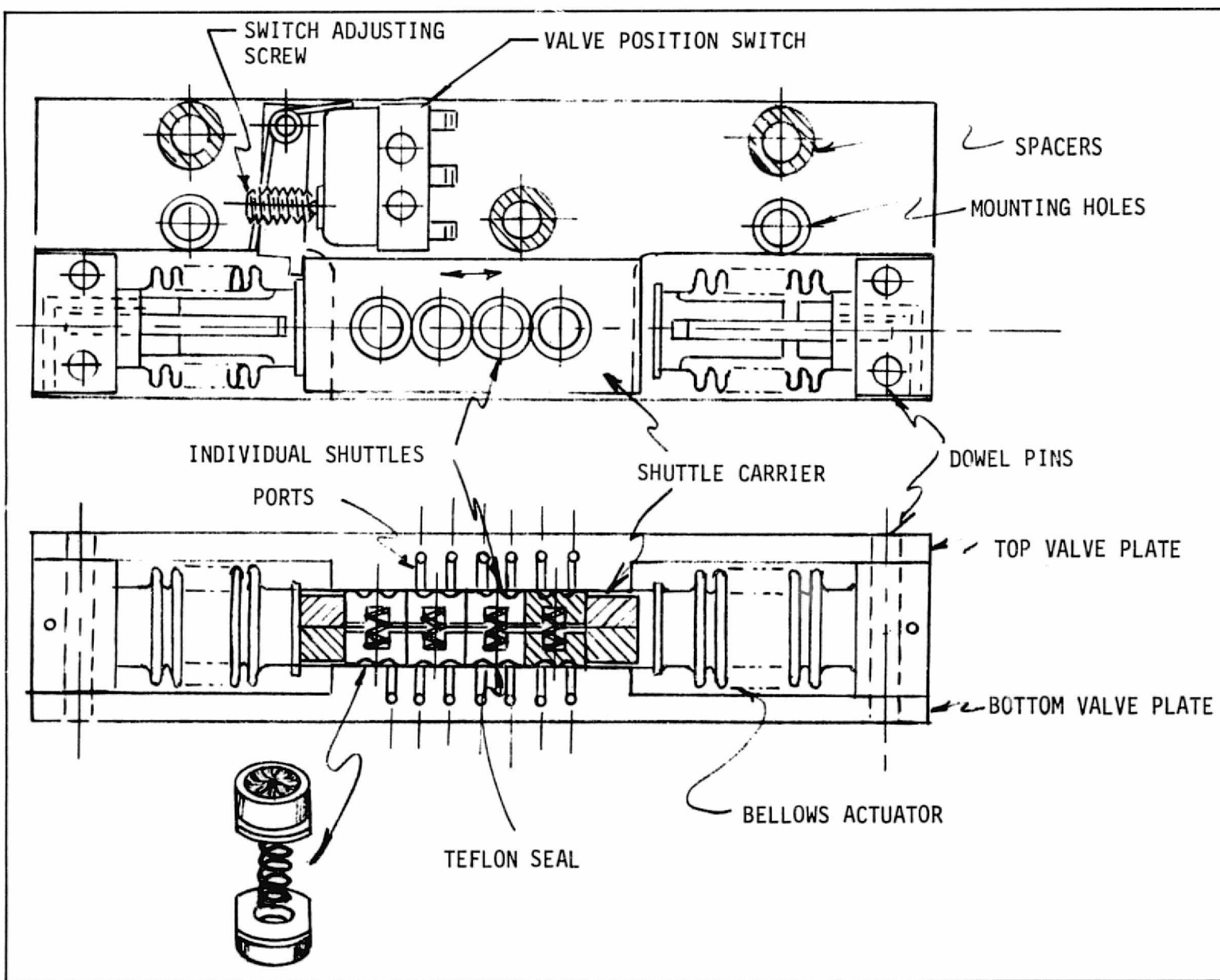


Figure 6-6. TGA Slider Valve

per second. We believe that this was due to diffusion through the Teflon film itself. Vespel SP-1 was then chosen because of its lower permeability.

We found that the Vespel poppets must be preselected because the Vespel contains minor impurities which tend to scratch the polished valve plate surface. Each Vespel poppet is tested for its ability to scratch a 316 stainless-steel plate. If it does not scratch the 316 plate, it will not scratch the harder 440C plate.

6.4.3 Effluent Divider

The effluent divider was made using spare valves and restrictors of the design developed on the Viking program. The technology for the assembly of the restrictors and low volume manifolds and tubing was also developed by Beckman for the Viking program. These valves, restrictors, and manifold assemblies are flight qualified. The valves are fast response, low volume, magnetic latching (low power) and have a built-in status switch. The restrictors are rod-in-tube type, which are accurate and stable when temperature controlled. The manifolds are small and contain almost no trapped volumes. The entire assembly is semi-inert because it is made of stainless steel and mounts in the thermal zone, which is held within $\pm 1^{\circ}\text{C}$.

The pressure upstream of the effluent divider is kept constant and above atmospheric pressure by matching restrictors R4 and R6 during calibration (FIGURE 6-7). After this upstream pressure was set, the split restrictors R5 and R7 were calibrated. The hydrogen that is diverted through V6 is reclaimed by a second separator.

The effluent divider protects the MS from pressure overloads by diverting a portion of large samples. The concentration of these large sample components can be determined because their MS signal is reduced by a known amount by fixed restrictors. Thus, the effluent divider significantly extends the system dynamic range.

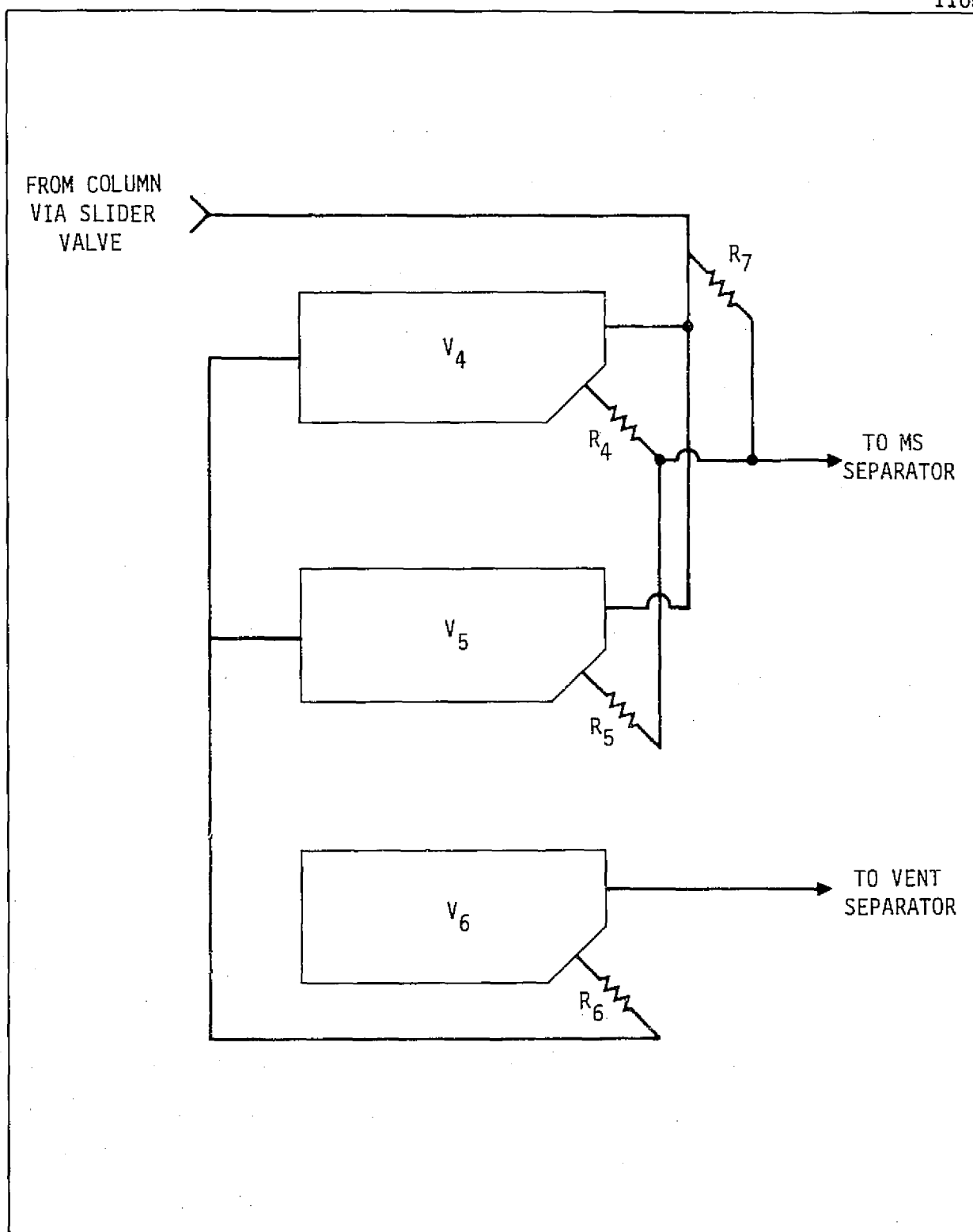


Figure 6-7. Flow Diagram of Three-State Effluent Divider

The effluent divider is a required part of the GC system because large sample components (nitrogen, oxygen, and carbon dioxide) would disable the MS ion pumps if not diverted. A one-stage divider (constant split ratio) could not be used because of the greatly varying sample concentrations and the need for maximum sensitivity for sample components at very low concentrations.

The following split ratios are used in the breadboard:

- 1:1--all sample flow into the MS (valves V4 and V5 open; V6 closed).
- 20:1--5% of sample flow into the MS (valves V5 and V6 open; V4 closed).
- 8000:1--protects MS from sample flow with up to 100% concentration (valves V6 open; V4 and V5 closed).

For maximum sensitivity all sample is directed toward the MS. As the sample concentration increases, the pressure level in the ion source increases. When a pressure of 21 MPa (1.6×10^{-5} torr) in the source is exceeded, the source response becomes nonlinear. Assuming a triangular-shaped GC peak, 15-s wide at half-height resulting from a 0.5-ml sample volume, and assuming a source conductance of 50 ml/s, a sample concentration of 40 ppm results in this 21 MPa (1.6×10^{-5} torr) ion source pressure. For sample concentrations between 40 and 1600 ppm, the effluent divider could be switched to the 20:1 split ratio. This ratio was chosen for several reasons. One is because a 41-ppm sample component could still be detected and measured by the MS. Another is because maximum source pressure would correspond to a sample concentration of 1600 ppm, which is higher than the maximum sample concentration expected (except for N₂, O₂, and CO₂). Therefore, only a three-stage effluent divider is required compared to the four-stage used on the Viking GCMS.

The restrictor manifold assembly is vacuum-furnace-brazed to minimize contamination. The collars for the GCMS fitting are torch-brazed with flux and then cleaned with hot deionized water. The tube is purged with a clean dry gas (helium, nitrogen, argon) to prevent oxidation and contamination.

The old design of the restrictor with a single pin in the tube was tried and found to continue to drift with valve cycles. A modified restrictor was constructed using a dual pin in the tube. It was found to be stable with valve

cycles (FIGURE 6-8). The short outer pin acts as a shock absorber when the upstream valve is cycled. This design was used on all restrictor units.

After assembly, the effluent divider was calibrated on a fixture that holds valves V4, V5, and V6, connecting restrictors R4, R5, R6, and R7, and manifolds M1, M2, and M3. A "hot" calibration was performed with flow (dynamic). The calibration was similar to the procedure for setting the high-pressure restrictor. The desired value was approached slowly. The assembly was heated (230°C to ambient) and valves were cycled between adjustments. Final calibration of the TGA breadboard effluent divider was performed at 205°C and 84.1 kPa (12.2 psig). This was done before raising the T-zone temperature to 220°C, to allow a greater safety factor in separator operation.

With a 84.1 kPa (12.2 psig) upstream of the effluent divider, the final restrictor values were:

- 1:1 Flow is 4.0 std ml/min to MS
- 20:1 Becomes 15:1--1 part in 15 to MS
- 8000:1 Becomes 8900:1--1 part in 8900 to MS

The unit was then ready for installation in the T-zone.

6.4.4 Carrier Gas Separator

The separator interfaces the GC with the MS. It removes nearly all the carrier gas, which allows the MS to operate on a small ion pump and allows 100% of the sample to be transmitted to the MS if desired. The recirculating hydrogen system reclaims the hydrogen which decreases required storage volume and eliminates the problem of disposing of the hydrogen.

The electrochemical separator developed for the Viking GCMS is completely flight qualified and the design is documented; its use on the TGA breadboard required no development effort. A functional diagram of the separator is shown in FIGURE 6-9. It removes hydrogen by using an electrolyte as the oxidizing medium, which reduces the partial pressure of hydrogen to near zero when a

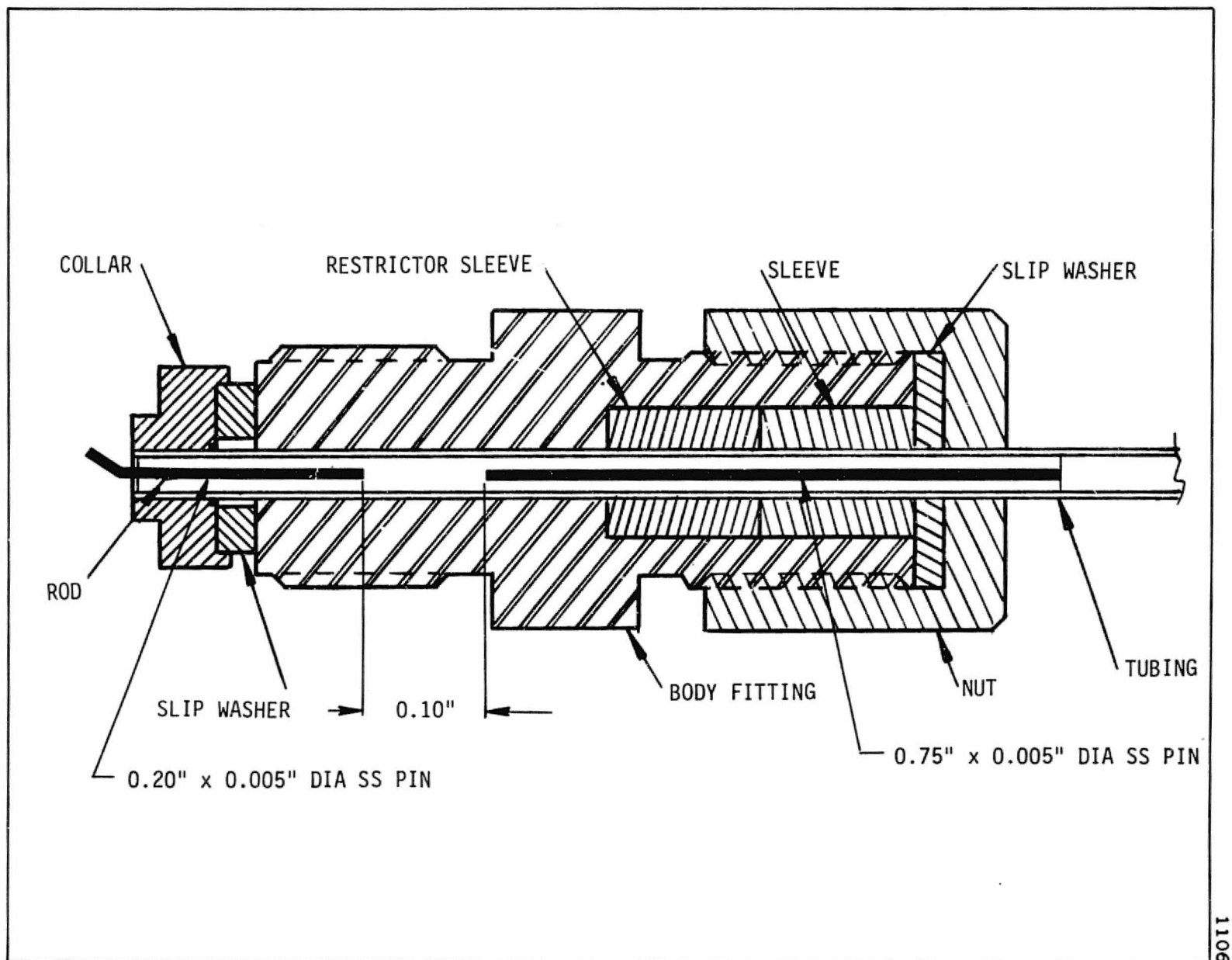


Figure 6-8. Rod-In-Tube Restrictor

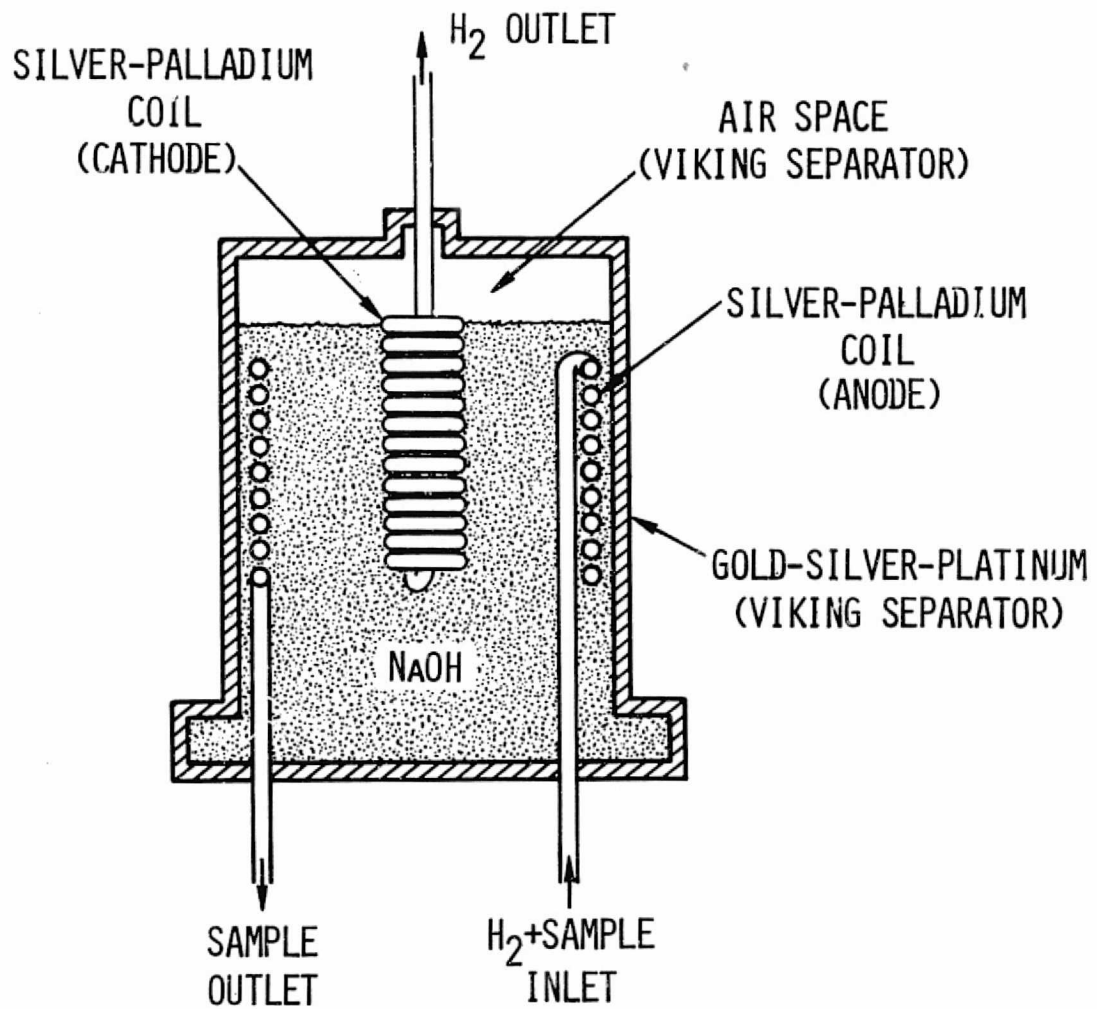


Figure 6-9. Hydrogen Separator Construction

potential is applied. The concentrated sodium hydroxide (NaOH) electrolyte is prepurified in a Teflon container by using platinum electrodes to plate-out the impurities. The electrolyte melts at about 160°C and therefore is liquid at its operating temperature of between 200° and 225°C (+1°C). The operating potential of 0.6 to 0.7 V, when applied to the separators, will theoretically pressurize the cathode assembly to 82.7 MPa (12,000 psi). The GC system has the cathode (vent) tubes attached upstream of the flow control restrictor and shutoff valve (1.38 to 1.72 MPa, or 200 to 250 psig) which allows the carrier gas to be recycled.

Tests conducted at Beckman (and previously at the Jet Propulsion Laboratory) with the system shown in FIGURE 6-10 have demonstrated that the electrochemical separator does pressurize hydrogen as theory predicts. Pressures up to 6.89 MPa (1000 psi) have been easily obtained without any performance degradation. Tests in our laboratory have shown that no hydrogen leaks between cathode and anode tubes when the separator has been cooled to ambient and the potential removed (a cooled separator is like a closed valve).

The requirement for the TGA separation differs from those of the Viking Mars Lander. The TGA must operate in zero gravity. The present Viking electrochemical hydrogen separator meets these requirements and was used in the TGA breadboard with only a minor modification in assembly procedure. Because the Viking separators are not completely filled with electrolyte, an air space exists that could bridge the gap between anode and cathode if used in the zero gravity of the Shuttle or under back pressure. Therefore, the separator used on this program must be completely filled with electrolyte at operating temperature. Our assembly procedure for separators was changed to eliminate the air space.

A second separator is located in the vent line to remove the hydrogen from the carrier gas stream when the effluent divider is in the vent position. If not reclaimed, the hydrogen would be lost to the spacecraft's environment. During venting by the effluent divider, a small amount of hydrogen will combine with oxygen that has diffused into the vent tube. The completed separator was

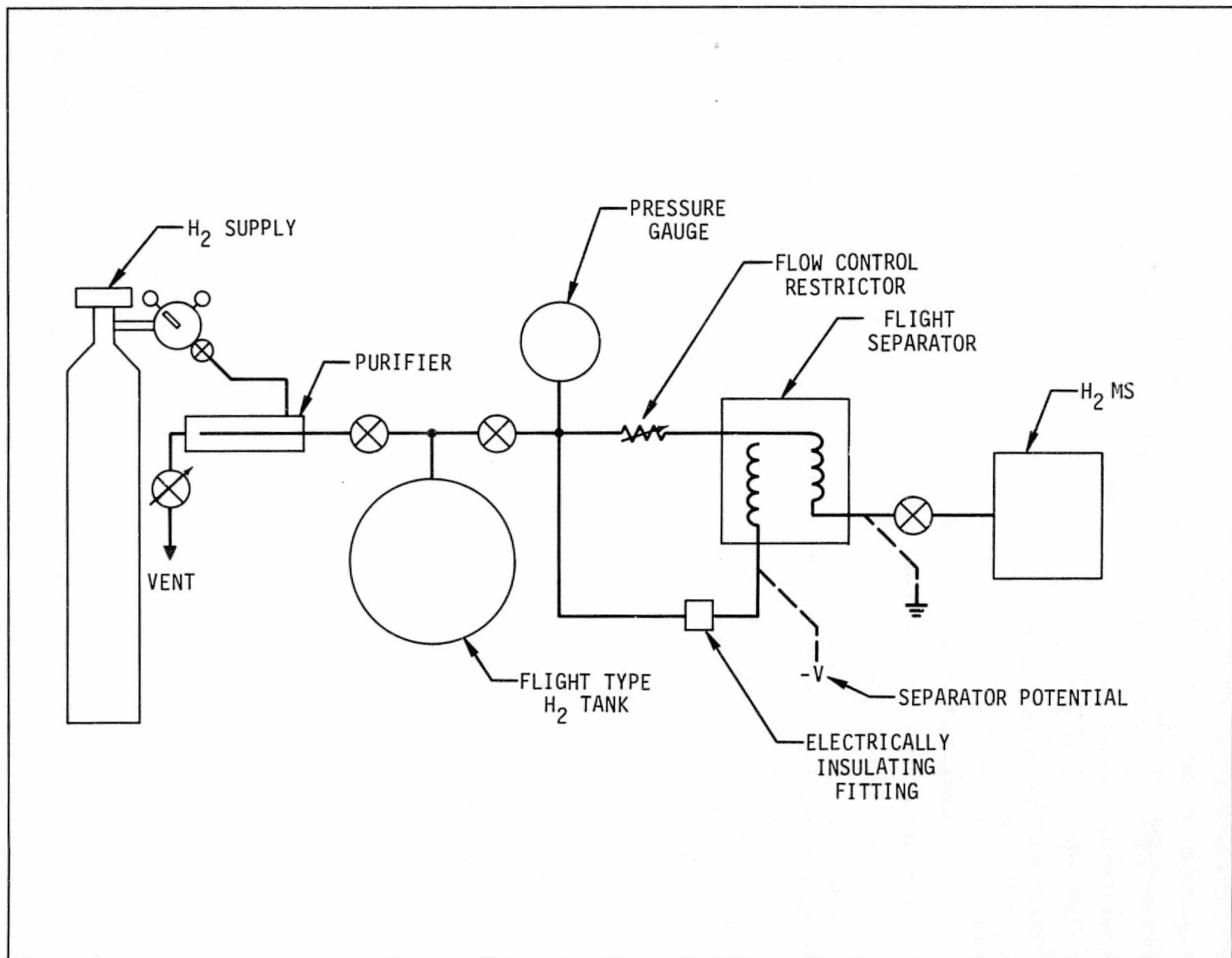


Figure 6-10. Test System for Recycling Hydrogen

tested to determine hydrogen removal efficiency before it was assembled into the T-zone. The transmitted hydrogen was measured with a mass spectrometer while the separator was receiving 4 std ml/min of hydrogen flow and with its vent line pressurized to 1.55 MPa (225 psi). The separator current was measured with and without pressure on the vent line to determine if any gaseous diffusion was occurring in the electrolyte.

6.4.5 Mechanical and Thermal Design

The existing Viking GCMS Thermal Zone was modified to accommodate the new Sample Valve and the additional Separator. The GC components in the Thermal Zone are maintained at a uniform 220°C to prevent sample condensation and to eliminate variation of restrictor flow ratios. The Viking Thermal Zone underwent extensive thermal analysis and testing to correctly size the power ratios of the six heaters and to optimize the location of valves and separators. Maximum use of this design analysis and experience was made for the TGA Thermal Zone (FIGURES 6-11 and 6-12).

The thermal characteristics of the Viking valves and separator are very similar. It was, therefore, possible in the TGA Thermal Zone to locate the required additional separator in an unused valve saddle without materially changing the thermal performance.

The slider valve was located on the end of the heated frame assembly within the Thermal Zone. One additional heater was incorporated due to the added thermal mass of this valve.

The thermal design maintained at temperature the many small tubes within the Thermal Zone by enclosing them between the heated frame and two inner Thermal Box covers. The new tubes associated with the Sample Valve are heated similarly, with a new Thermal Box end cover and extension of the outer box with additional thermal insulation. Low thermal conductivity standoffs provide the connection to the Sample Valve slider.

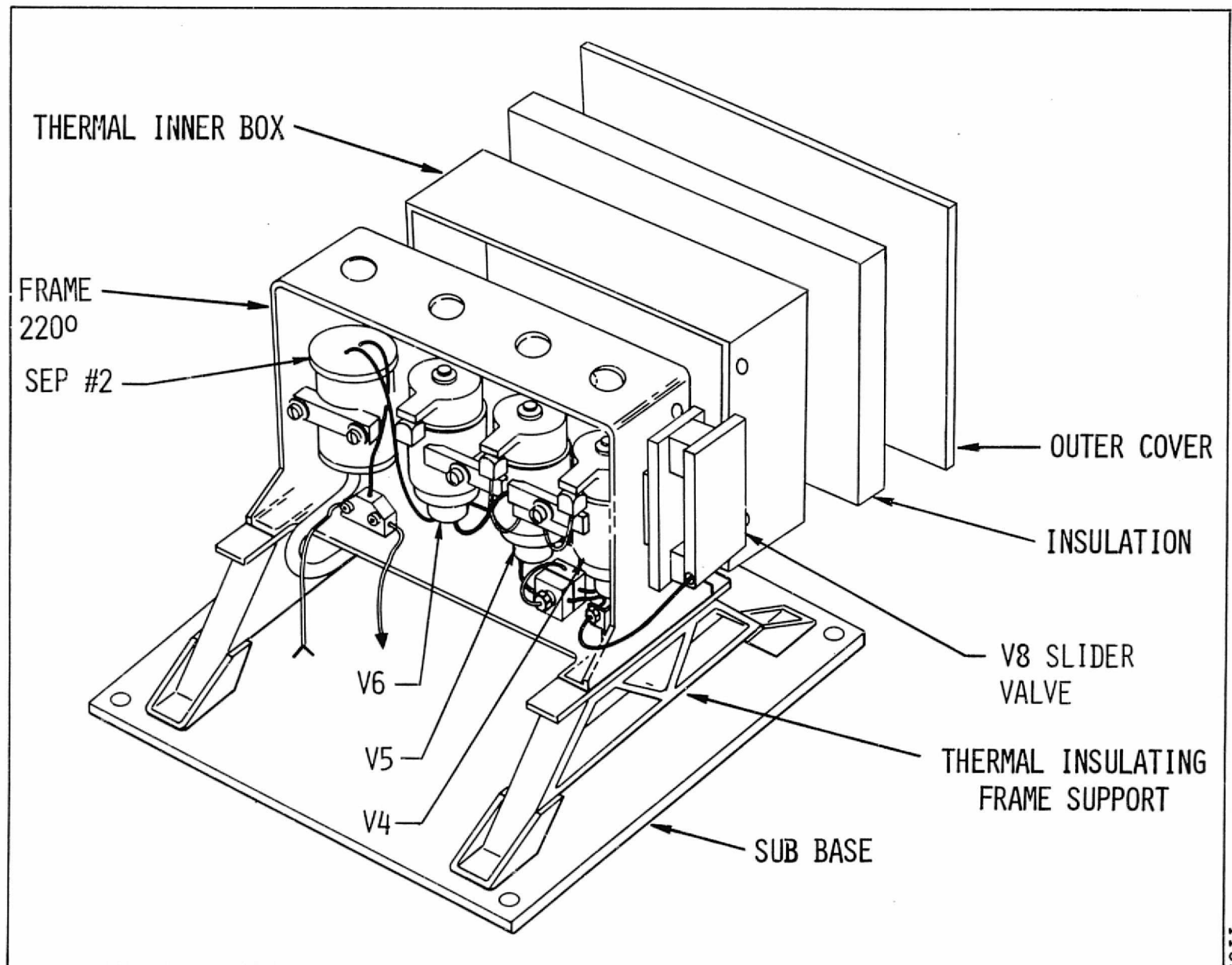


Figure 6-11. Thermal Zone Construction--Effluent Divider Side

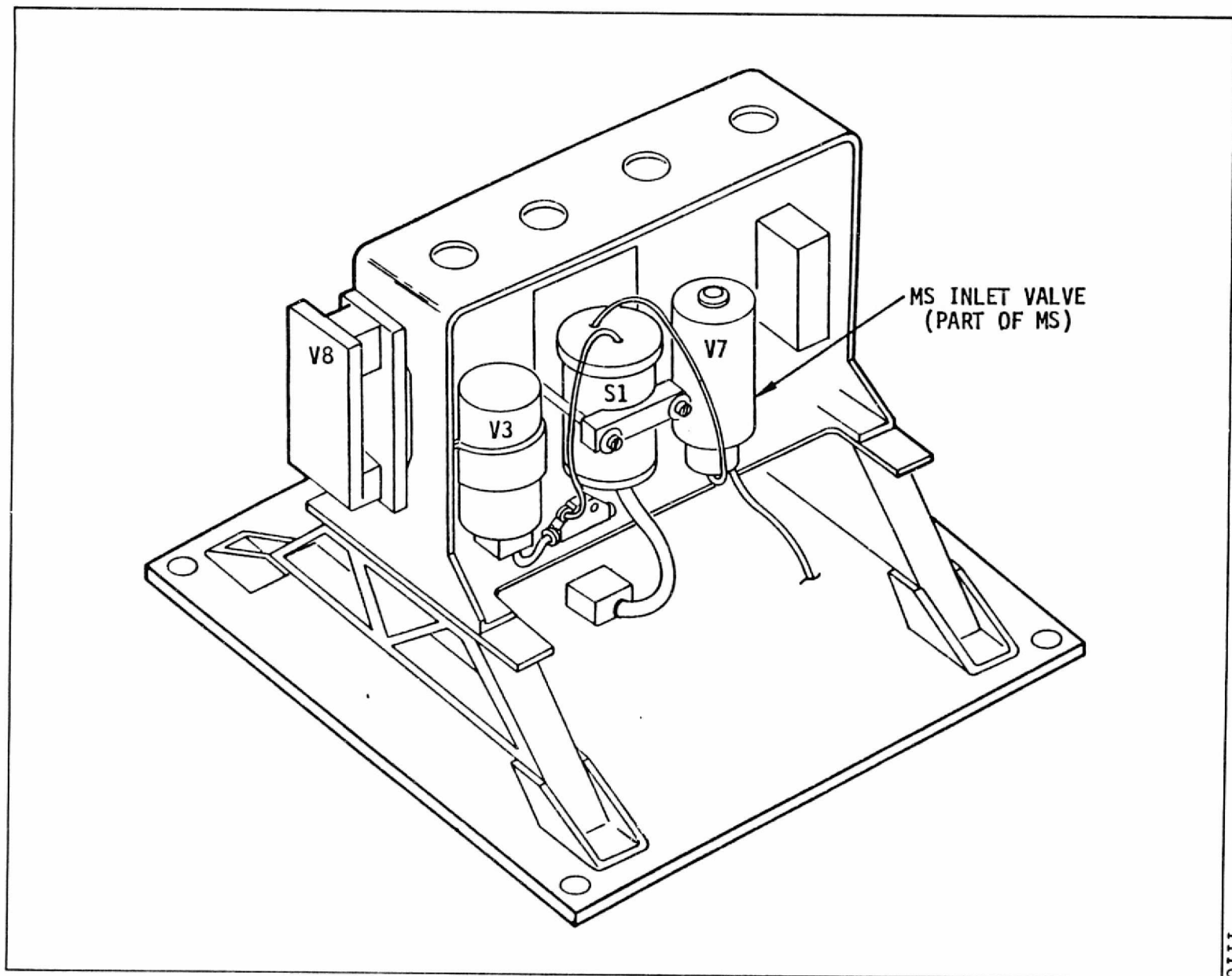


Figure 6-12. MS Side of Thermal Zone

6.5 Sample Pump and Sample Loops

6.5.1 Sample Pump

A small diaphragm pump was built into the system to make certain the sample loops contain a representative sample of the atmosphere being tested. This pump is a Spectrex Model AS-120-3, which has been used on Beckman CO analyzers. Measuring 4.76 x 4.76 x 6.99 cm (1-7/8 x 1-7/8 x 2-3/4 in.), the pump was tested to determine flow rates of air at various input voltages. A 1.83-m (6-foot) section of 0.51-mm (0.020-in.) ID tubing was used as a restrictor.

<u>Voltage</u>	<u>Flow Rate (std ml/min)</u>
4.5	51
5.0	80
5.5	92
6.0	104

This flow is adequate to pump an atmospheric sample into the sample loops.

6.5.2 Sample Loops

It was found desirable for the breadboard unit to package the sample loops in a different oven than the CO column, even though they nominally operate at the same temperature. Separate packages allow CO testing at different temperatures and accessibility for replacement of either CO column or sample loops. In the breadboard unit, the sample loops are 2.77-m (9.1-ft) long sections of 0.51-mm (0.020-in.) ID stainless steel tubing wrapped on an aluminum mandrel and heated with a cartridge heater. The temperature is controlled at 60°C by one of the line heater controllers. The connecting line length is about 0.46 m (1.5 ft) of 0.51-mm (0.020-in.) ID tubing. Therefore the total sample loop volume at 60°C is 0.5 ml.

6.6 GC Electronics

6.6.1 Design Approach

The GC electronics system consists of all the modular circuits that functionally control the effluent sample flow system, control various heated assemblies,

provide power for the effluent carrier gas separator system, and provide analog and digital information to the instrument data system.

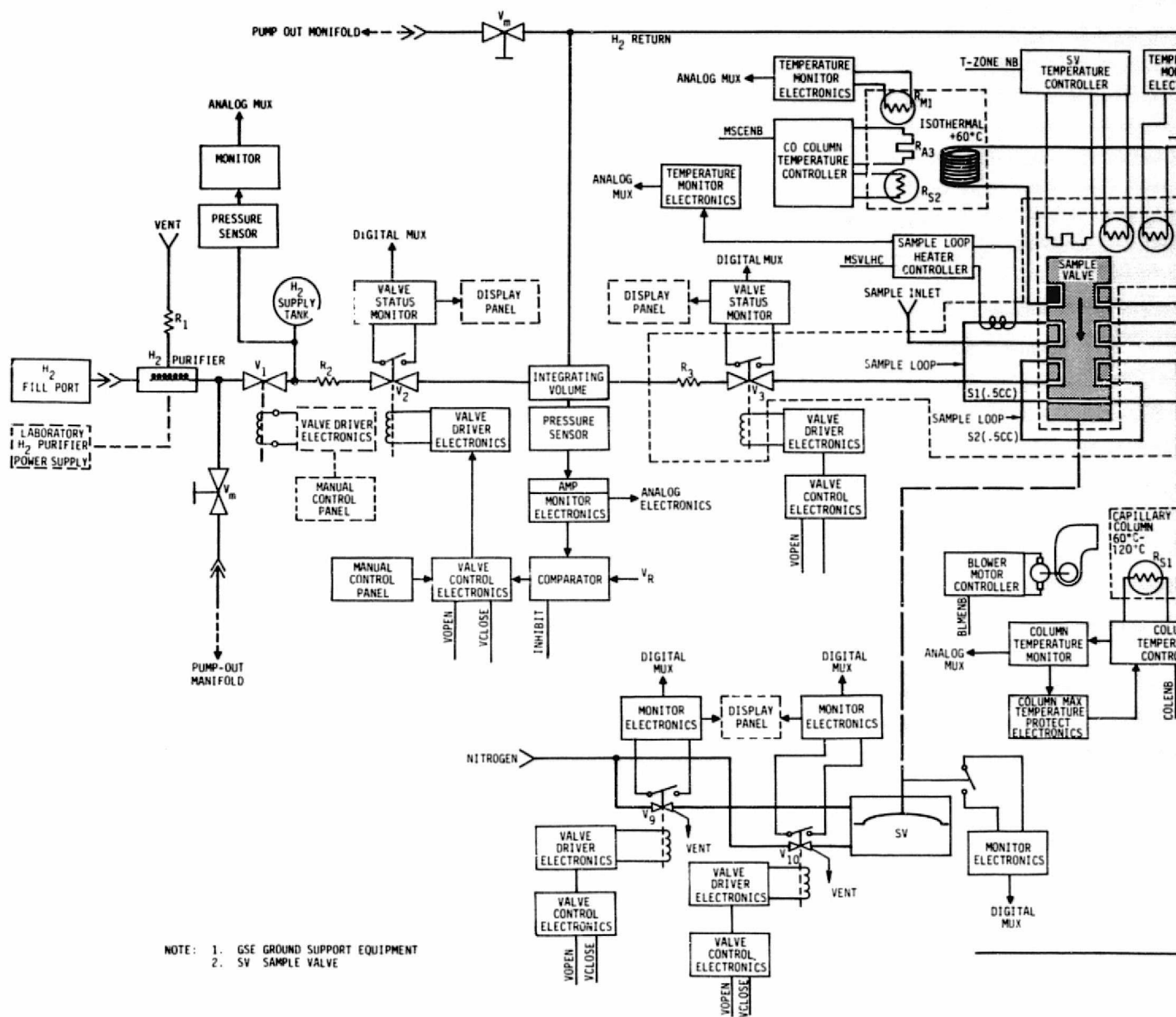
An overall electronic diagram is shown in FIGURE 6-13. Several of these circuits were modified by the addition of integrated circuits to protect the instrument during the sequence of manual operation.

All control valves, except the Sample Valve, are magnetic-solenoid, bidirectional, latching-type valve assemblies actuated by a current pulse. The valve actuation pulse width may be as short as 10 ms.

The temperature control circuits are of two types: on-off control, and proportional control. On-off controllers provide temperature control for the thermal zone assembly, line heater assemblies, and the isothermal packed column assembly. The organic column temperature controller is a proportional controller (variable duty-cycle controller), with the duty cycle programmed to increase the column temperature at a uniform rate. This controller was built and tested but was not used during breadboard tests since the column was not packaged in a final configuration and no column cooling fan was used.

The Hydrogen Separator power supply provides regulated voltage to both separator assemblies. The supply is current-limited to protect the supply and instrument power source from accidental short circuits during breadboard testing.

Analog housekeeping signals will be available for the temperature-controlled assemblies and the carrier gas flow rate. Also, analog signals, proportional to the carrier gas source pressure, are supplied to the instrument data system. Digital signals monitoring the status of each valve are supplied to the instrument data system. During testing the outputs of some meters were changed to display data in engineering units. For example, a volume-pressure reading of 2.17 volts indicates a pressure of 1.50 MPa (217 psi). Similar conversions were made for separator current (hydrogen flow) and temperatures.



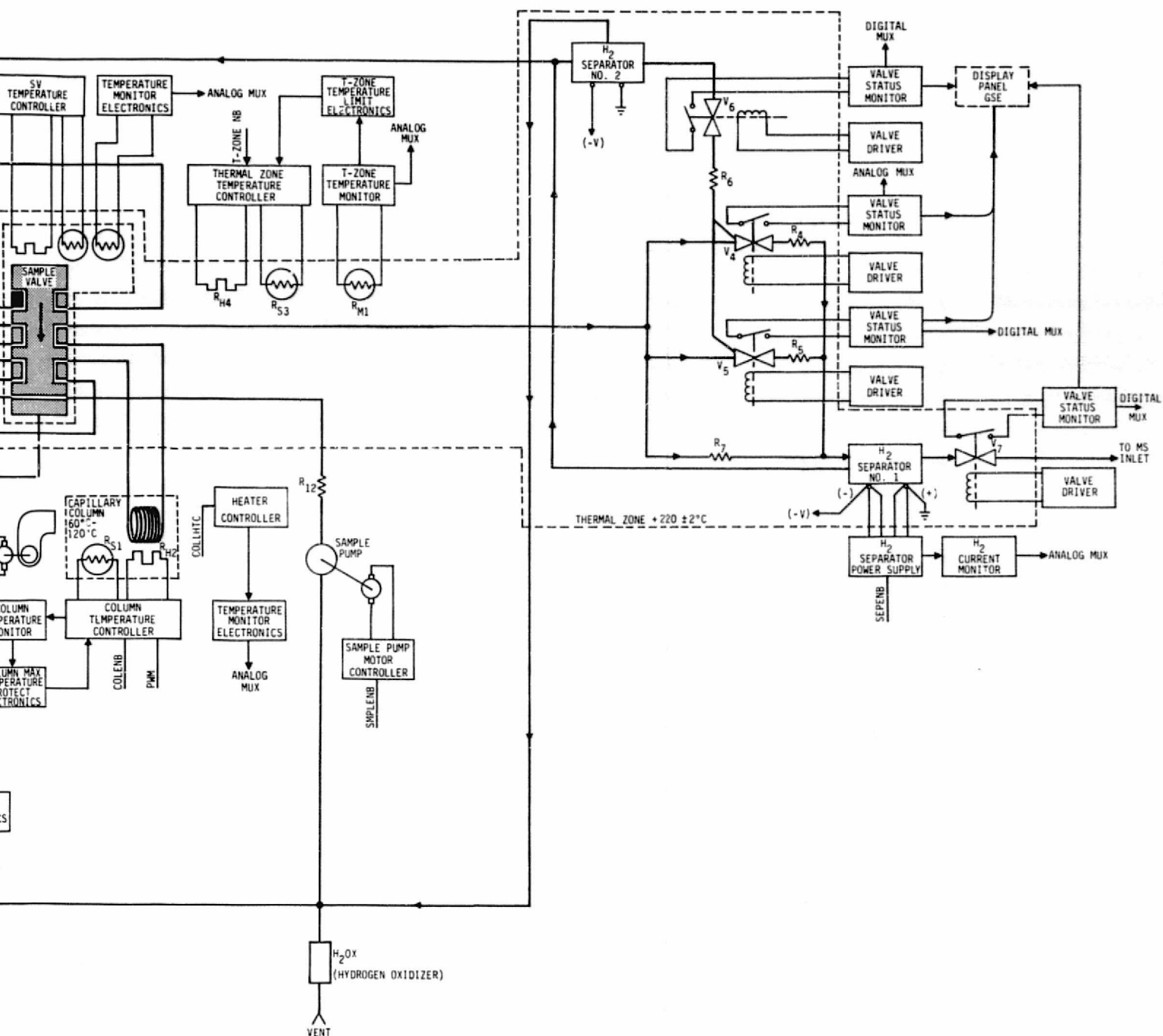


Figure 6-13. GC Analyzer Subsystem Flow and Electronics Block Diagram

The circuit design of the temperature controller, valve drivers, power supplies, and monitor circuits is similar to the circuits designed by Beckman for the Viking GCMS system.

Electronics for the GCS were built on vector boards and tested. The boards were then packaged in a rack--called an Omniclosure--and again checked out.

The vector boards--which had been tested individually--were placed in the card rack and tested as a separate system using decade resistance boxes to simulate heaters and sensors. An old Parker-Hannifin valve was used to check out the valve driver circuits. The card racks were mounted on a 48.2-cm (19-in.) panel with draw slides. The panels are shown in FIGURE 6-14.

For the breadboard, both the GC and MS electronics were mounted in a 1.83-m (6-foot) rack. This assembled rack is shown in FIGURE 6-15.

6.6.2 Carrier Gas Flow Rate Controller

The carrier gas pressure circuit controls the initial hydrogen pressurization of the equilibrium volume and carrier gas replenishment during the instrument operation. During the initial hydrogen fill cycle, carrier gas flows through the effluent sample system and recirculates to the hydrogen equilibrium volume. A pressure sensor monitors this pressure and actuates a valve control circuit closing the hydrogen supply valve (V2) at a preset pressure of 1.52 MPa (220 psi).

During the effluent analysis cycle, the hydrogen gas flow divides between hydrogen separator No. 1 and No. 2. Carrier gas from both separators is recirculated to the integrating volume. The hydrogen supply valve opens if the pressure drops below a minimum pressure set point (1.49 MPa or 216 psi).

The hydrogen supply valve control circuit consists of a pressure sensor, an amplifier and monitor circuit, a hysteresis comparator, control logic, and valve driver. Manual control of the valve circuit is supplied to override the automatic control system.

FIGURE 6-16 is a block diagram of the pressure sensor control loop. The pressure control point is 1.50 MPa (218 psig $\pm 1\%$). The low-level pressure

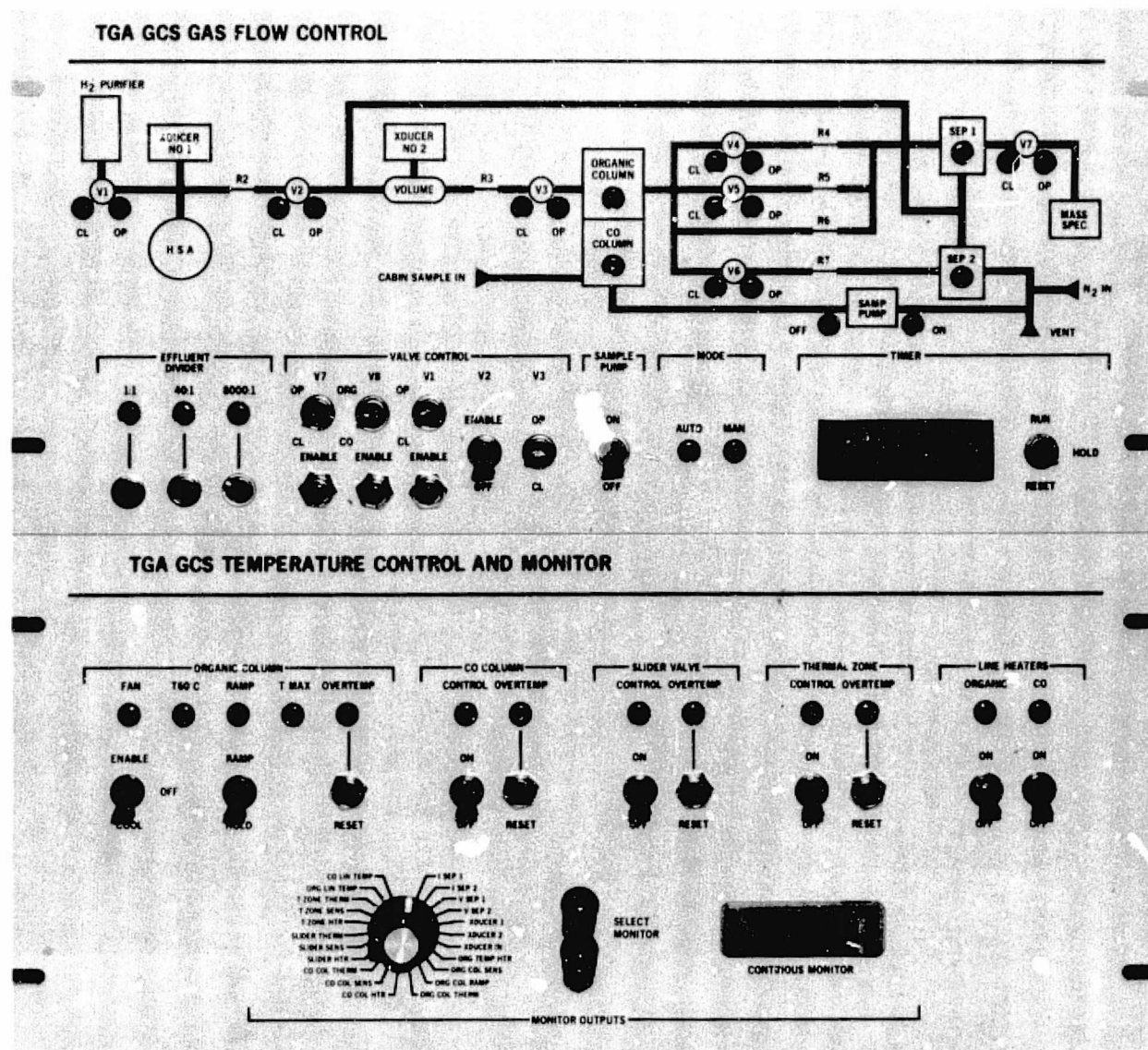


Figure 6-14. GCS Manual Control Panels

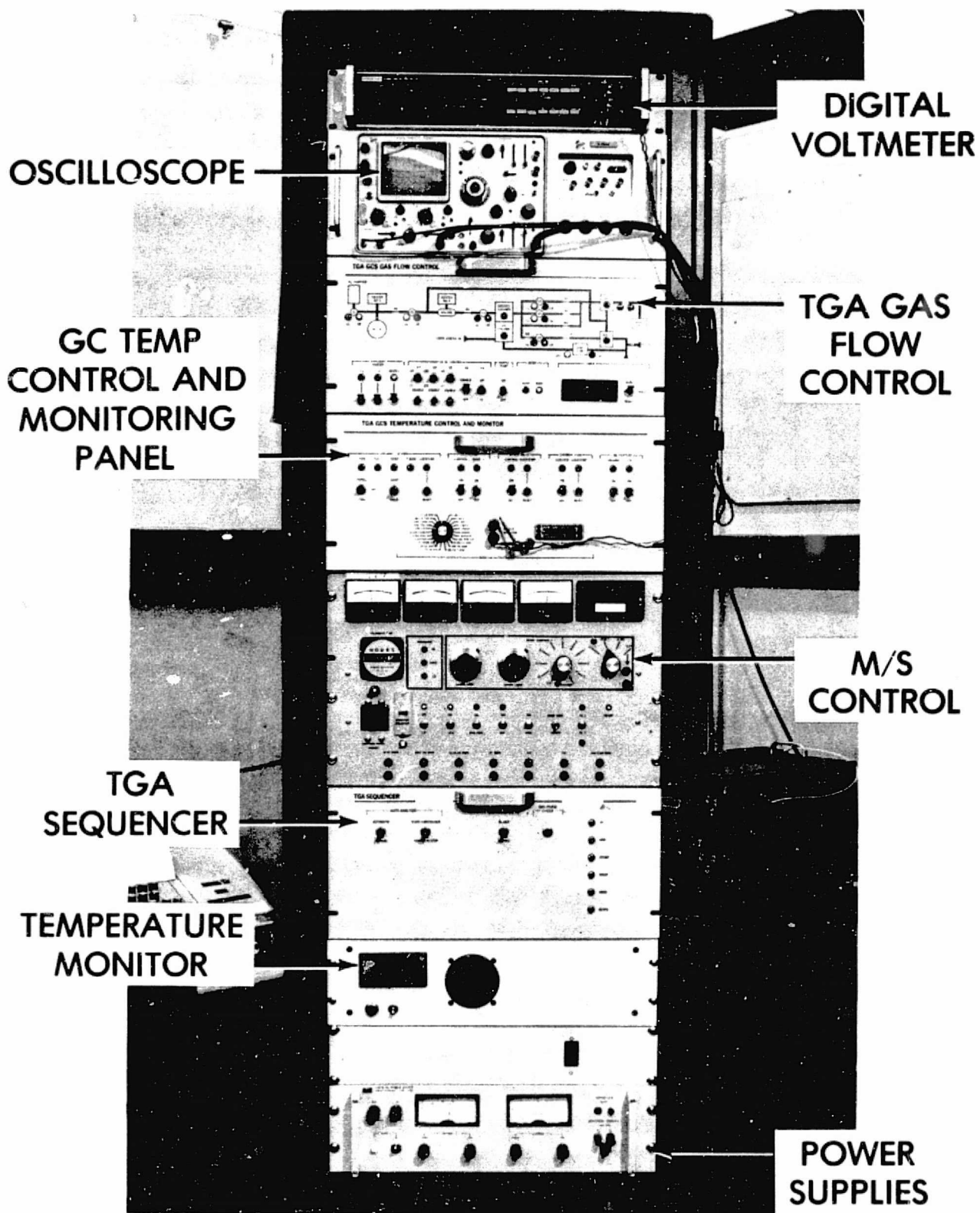


Figure 6-15. GC and MS Rack Module

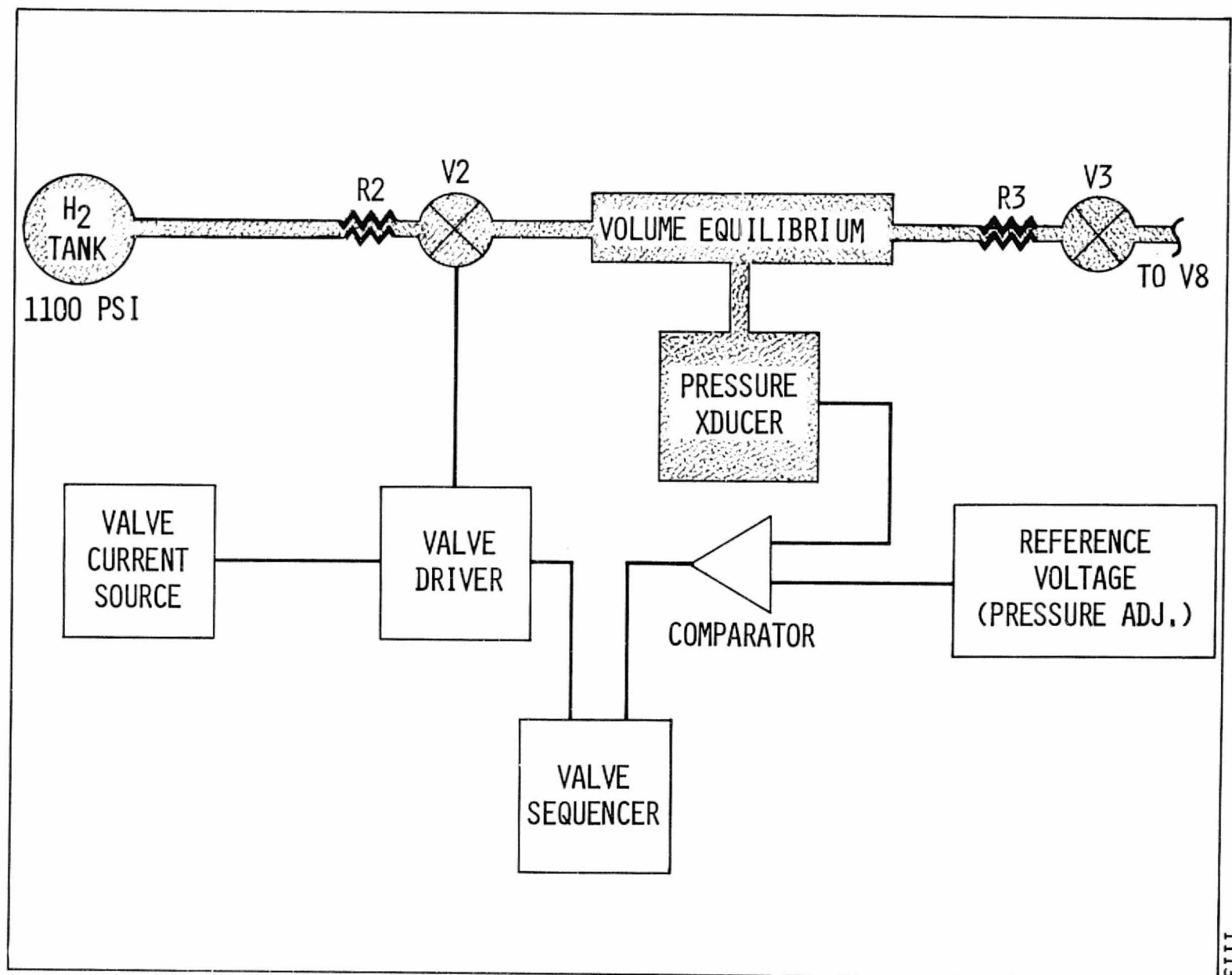


Figure 6-16. Servo System for H₂ Pressure Regulation

transducer signal is amplified and compared to the reference pressure voltage at the Comparator circuit, which generates a Set or Reset valve control command, driving the valve to latch open or closed as required.

6.6.3 Valve Control Circuit

The GC flow control valves are magnetic, bidirectional, latching valves programmed by command signals from the manual control panel on the system sequencer. Each valve is actuated by a single current pulse of 2.5 A, 12 ms duration (FIGURE 6-17). A valve status signal line (switch closure) for each valve is supplied to the sequencer and data system to provide flow information and sequencer feedback logic signals.

Valve power and control circuits are isolated from the logic system by use of transformer-coupled control lines and insulated switch status signal lines. Power from the valve control circuits is derived directly from the unregulated instrument power source.

Valve circuits were designed and packaged by Beckman for the Viking GCMS system.

6.6.4 Column Temperature Controller

The GFE column temperature-vs.-time profile typically specifies a 15- to 25-minute isothermal hold at +60°C, followed by a ramp increase to +120°C at a 2°C/min rate and hold at +120°C. A pulse-width-modulated control circuit provides excellent response characteristics for this application and is readily adaptable to logic programming.

A block diagram of the proportional control circuit is shown in FIGURE 6-18. The column temperature monitor circuit consists of a platinum resistance sensor, scaling amplifier, and buffer amplifier. The output signal from this circuit provides both engineering temperature information, analog data, and the feedback signal to the error detector amplifier.

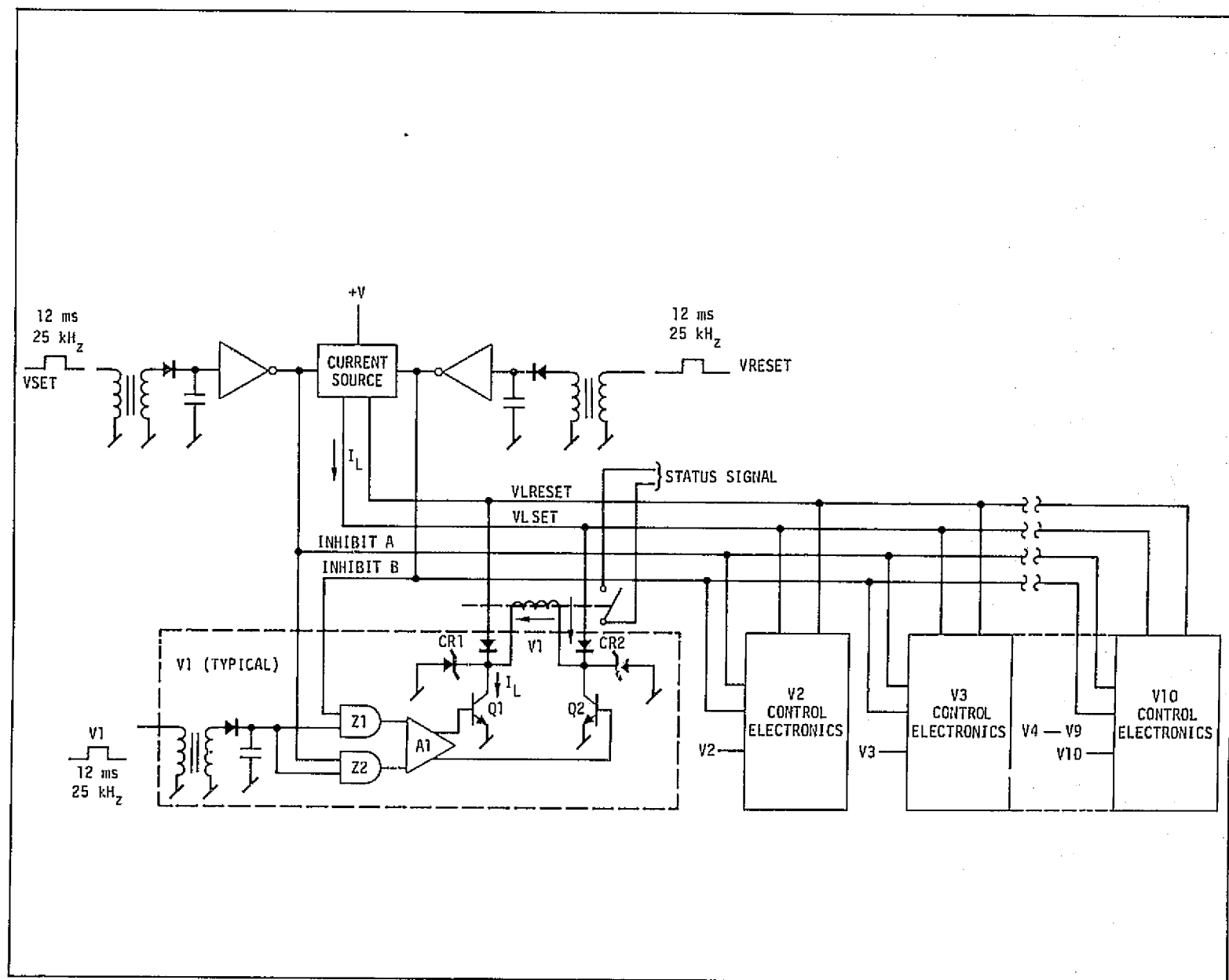


Figure 6-17. Valve Control Electronics

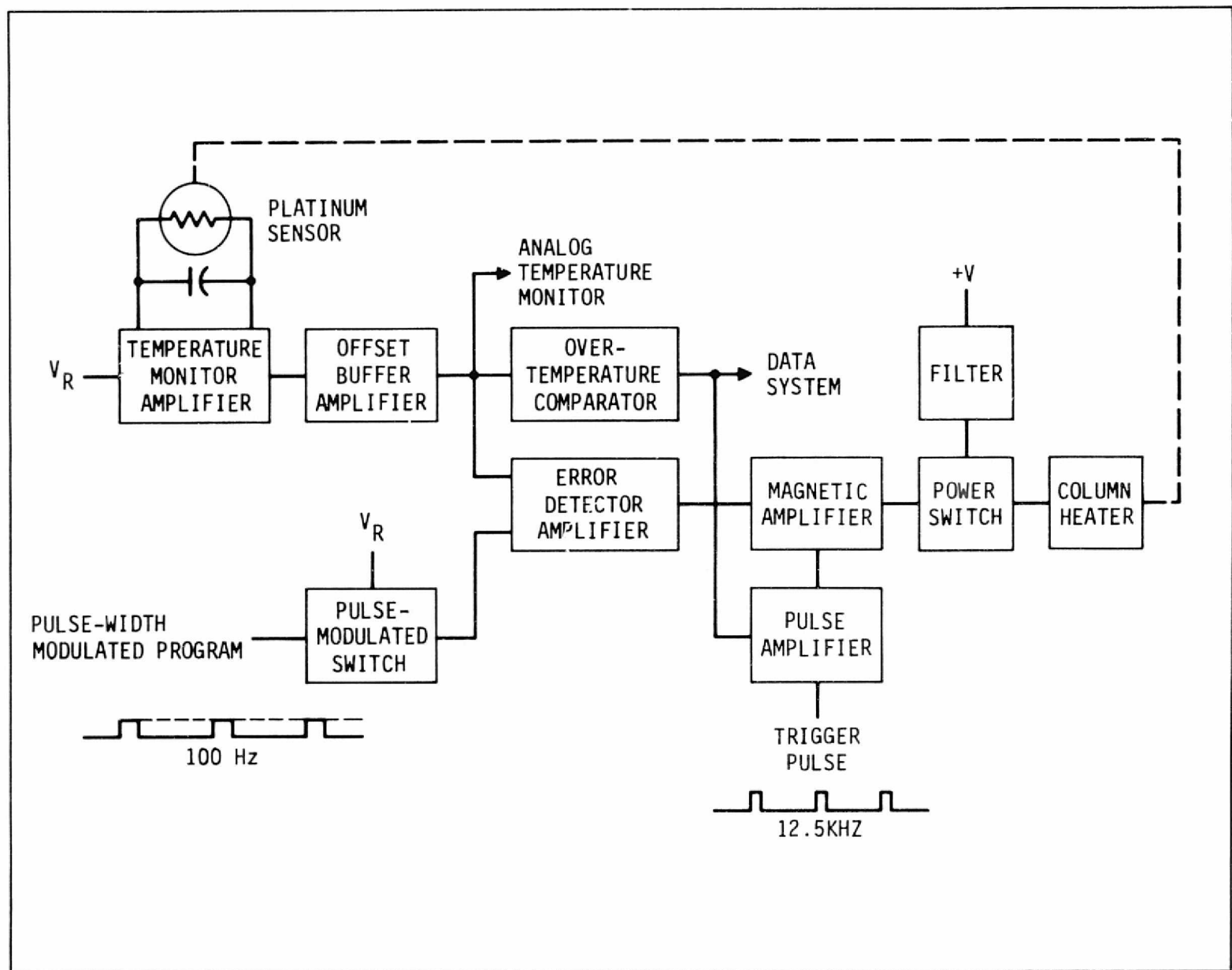


Figure 6-18. GFE Column Temperature Controller Block Diagram

This controller was built and tested but is not used since the organic column was not packaged in a flight configuration.

The column over-temperature monitor circuit automatically resets the temperature program to minimum temperature, disables the temperature controller, and enables the column cooling blower (when employed).

With the instrument control in MANUAL or AUTOMATIC mode, the column temperature can be ramped at the nominal rate of $2^{\circ}\text{C}/\text{min}$ and/or held at any intermediate temperature between 60° and $+120^{\circ}\text{C}$.

6.6.5 Thermal Controllers

Several independent programmed temperature controllers are required for the GC Subsystem. Each of the controllers operates at a different temperature. Separated heater controllers are required for the Thermal Zone assembly, CO column assembly, sample valve assembly, sample loops, and permeation tube oven. All controllers are on-off type control circuits, using a thermistor or platinum resistor for the feedback sensor.

A block diagram of the thermal zone, slider valve, and CO column controller is shown in FIGURE 6-19. The temperature for each is monitored by a platinum resistor sensor mounted adjacent to the heater in the assembly. This sensor is connected as one leg of a dc bridge circuit.

The control temperature is adjusted by trimming resistors in the reference leg of the bridge circuit. The bridge dc error signal controls the logic inputs to a J-K flip-flop that is clocked at a frequency of 1 Hz. The flip-flop output gates a 25-kHz clock signal that is transformer-coupled to the heater driver circuits. Transformer coupling is required to isolate the heater switching currents from instrument analog and signal grounds. Fold-back current limiting is provided to disconnect heater loads from the instrument power buss in the event of heater short-circuit failure.

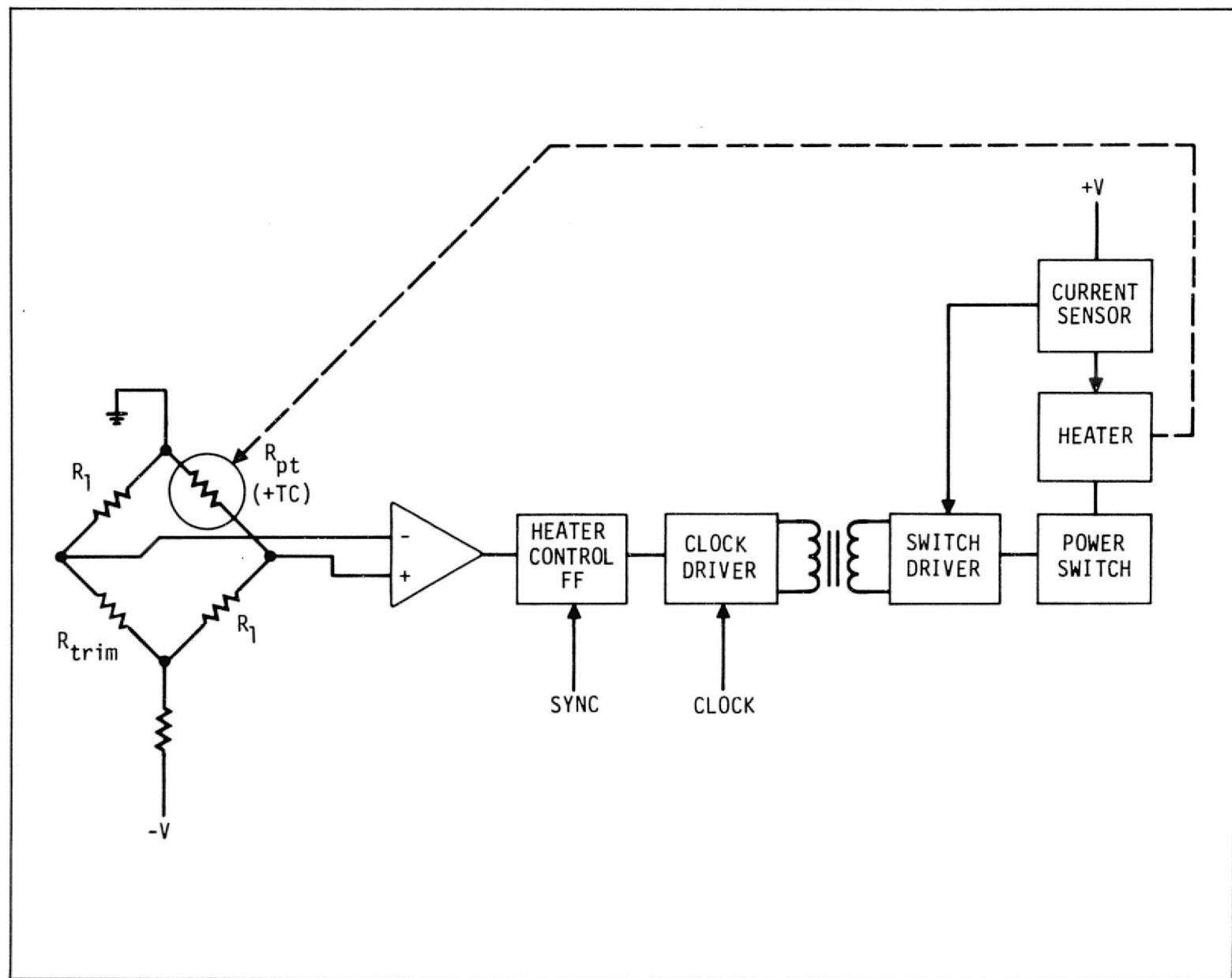


Figure 6-19. Temperature Controller for Thermal Zone, Slider Valve, and GC Column

The temperature controller block diagram for the sample loops and permeation tube oven is shown in FIGURE 6-20. The operating temperature is set at +60°C. The temperature is monitored by a thermistor sensor mounted adjacent to the heater element in the column assembly and connected to one leg of a dc bridge circuit, as shown. Operating temperature is set by adjusting the trimmer resistor in the lower leg of the bridge circuit. The temperature controllers are manually enabled by front panel switches.

6.6.6 Separator Power Supply

Two hydrogen carrier gas separators are mounted within the Thermal Zone. Power for both units is supplied from a single 0.625-V source. The separator dc transfer function is a 143-mA supply current at a 1-ml/min hydrogen flow rate. With a flow rate of 4 ml/min, the nominal supply current was 572 mA. Initial turn-on current surges may exceed 800 mA; therefore, the supply current limiting was adjusted for approximately 1 A.

The circuit consists of a reference voltage, voltage regulator error amplifier, series regulator transistor, current sensing resistor, current monitor, and current limiting circuit. The current monitor signal supplied to the Data Subsystem provides the engineering signal to monitor the GC carrier gas flow rate.

6.6.7 Effluent Divider Status

Status information for each valve in the effluent divider assembly is provided by an electrically isolated switch on each valve. Switch closures correspond to valve closures. Pull-up resistors on each status line provide the signal current to the logic sequencer inputs. The logic signals trigger various logic sequences as required for control of the gas flow system.

6.6.8 Power Supplies and Power Distribution

For the TGA GC breadboard system, instrument power is supplied from commercial laboratory supplies. Supply voltages are +12 Vdc, -12 Vdc, +5 Vdc, and +28 Vdc.

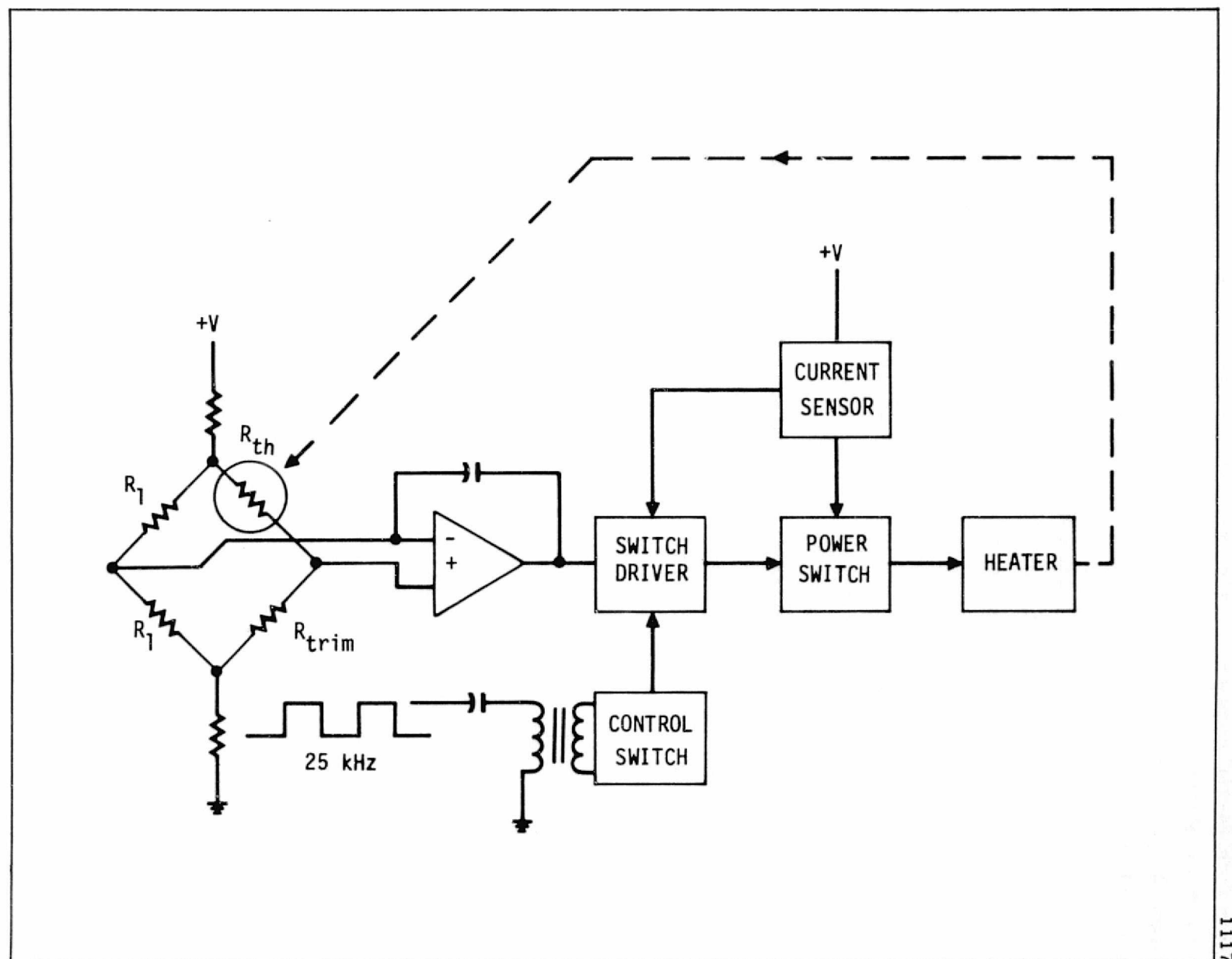


Figure 6-20. Temperature Controller for Sample Loops and Permeation Tube Oven

Heater controllers and heater elements operate directly from the +28 Vdc supply. The logic system and motor control circuits operate from the +5 Vdc supply. Analog control circuits and analog monitor circuits require +12 Vdc and -12 Vdc power for operational amplifiers and CMOS circuitry.

6.6.9 Motor Controllers

Two motor controller circuits are required for the flight GC Subsystem--one for the gas sample pump controller and the other for the capillary column cooling motor. Neither of these circuits was required for the TGA breadboard.

6.6.10 Instrument Sequencer

An Intel 8008 microprocessor and its peripheral equipment are used as the GC instrument sequencer. A separate drawer in the electronics rack houses the microprocessor and other equipment, including lamp drivers and manual selecting switches. This microprocessor is programmed to automatically operate the TGA breadboard.

7.0 BREADBOARD MASS SPECTROMETER SUBSYSTEM

This section describes the mass spectrometer subsystem used for the breadboard TGA. It includes a detailed discussion of the analyzer, the MS subsystem electronics, and the breadboard MS subsystem performance.

7.1 MS Subsystem Description

The MS subsystem consists of two major elements; the analyzer and the mass spectrometer electronics. These elements are not only distinctly different in function and nature, but also differ in terms of design considerations, assumptions, and approach. The following discussion of the analyzer emphasizes the description of the existing Viking analyzer and its performance parameters. The MS electronics are also largely based on the existing Viking circuits but there is a substantial impact at interfaces. Consequently, detailed discussion is provided regarding design criteria in the areas such as the MS control electronics, output electronics, data conversion electronics, and the scan and scan control circuitry. The selected approaches were based on detailed trade-offs in the critical areas such as the scan supply and output electronics.

7.2 Description of the Analyzer

The analyzer consists of that part of the MS subsystem that receives the sample from the separator in the form of a GC peak or gas flow pulse, ionizes a portion of the sample gas molecules, resolves these ions according to their mass-to-charge ratios, collects, amplifies, and outputs the resulting ion currents in the form of a mass spectrum, and pumps the remainder of the sample gas to maintain the internal vacuum. The elements of the analyzer required to accomplish these tasks are the sample inlet system, analyzer envelope including the electrostatic and magnetic sectors, ion source, electron multiplier, and ion pump.

7.2.1 Analyzer Description

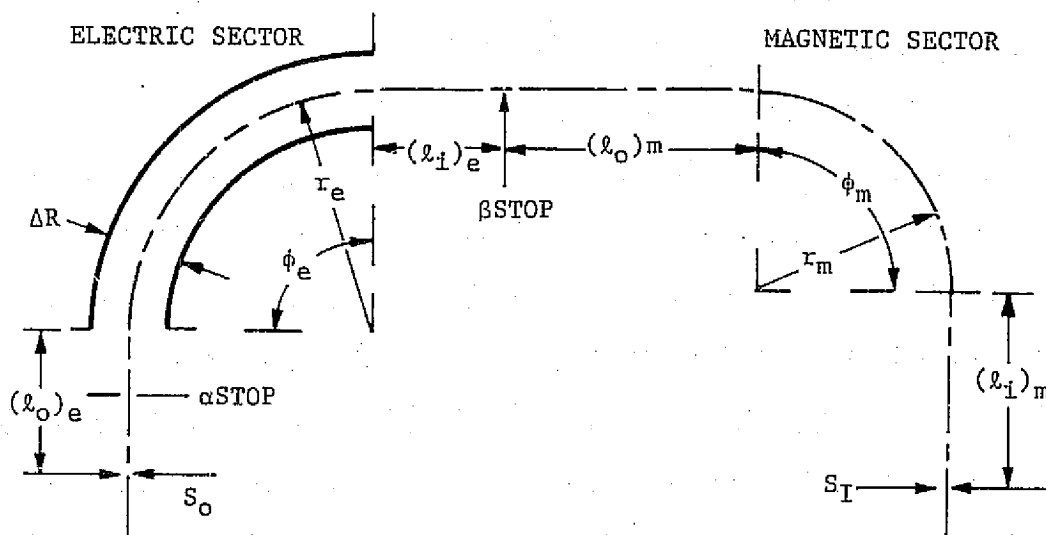
The mass spectrometer analyzer is a 90-degree electrostatic, 90-degree magnetic sector, Nier-Johnson configured instrument. The design parameters for the instrument are summarized in TABLE 7-1, and an outline drawing of the instrument is shown in FIGURE 7-1. The instrument has an ion source with its electron beam magnetically constrained. It is equipped with an ion pump which is integral at the magnetic sector. A single magnet assembly provides the field for the analyzer and the ion pump. The resolved ion current is detected by an electron multiplier tube.

7.2.1.1 Ion Source

The ion source is shown in detail in FIGURES 7-2 and 7-3. This dual filament source is designed to interface with the analyzer, providing minimum energy spread in the ion beam. The source has two filaments to provide redundancy. The filaments are 0.076-mm (0.003-inch) diameter tungsten-3% rhenium wire and are positioned slightly off-axis to the electron beam entrance cone, and an electron focus lens system is used to direct the beam into the ionization region through a low conductance aperture. A 600-gauss cylindrical magnet contained within the source mounting block constrains the angular spread of the beam through the ionization region. The end of the magnet extends around the filament region, and forms part of the electron focusing system. The electron beam walks in the extraction field (between the repeller and the saddle lens) at an angle of approximately 2 degrees with the optic axis of the analyzer. The source is tilted to align the beam with the optic axis. Most the electron beam is collected at the anode which is placed behind the exit slit from the repeller. Emission is regulated on total electron beam current, which is measured on all surfaces in the source.

Gas enters the instrument through a tube in the mounting block, flows around the mounting block, and enters the source through the ion exit aperture in the cylindrical magnet. The conductance of the modified source is approximately 5° ml/s at 20°C.

TABLE 7-1. DOUBLE FOCUSING MASS SPECTROMETER CONFIGURATION



$(\ell_o)_e$ = object distance, electric sector = 1.656 cm (0.652 in.)

$(\ell_i)_e$ = image distance, electric sector = -1.656 cm (-0.652 in.)

$(\ell_o)_m$ = image idstance, magnetic sector = 2.568 cm (1.018 in.)

r_e = radius "optical axis", electric sector = 4.724 cm (1.860 in.)

r_m = radius "optical axis", magnetic sector = 3.818 cm (1.503 in.)

S_o = object slit width = 0.051 mm (0.002 in.)

S_I = image slit width = 0.051 mm (0.002 in.)

α_o = angle spread in beam $\pm 1.2^\circ$

$\Delta V/V$ = energy spread in beam = ± 0.1 max (normalized)

β_o = velocity spread in beam = $v_o/v_o = \pm 0.0067$ max

M_m = magnification in magnetic sector = -0.68

ΔR = electric sector gap width = 3.175 mm (0.125 in.)

g = magnet gap width = 2.540 cm (0.100 in.)

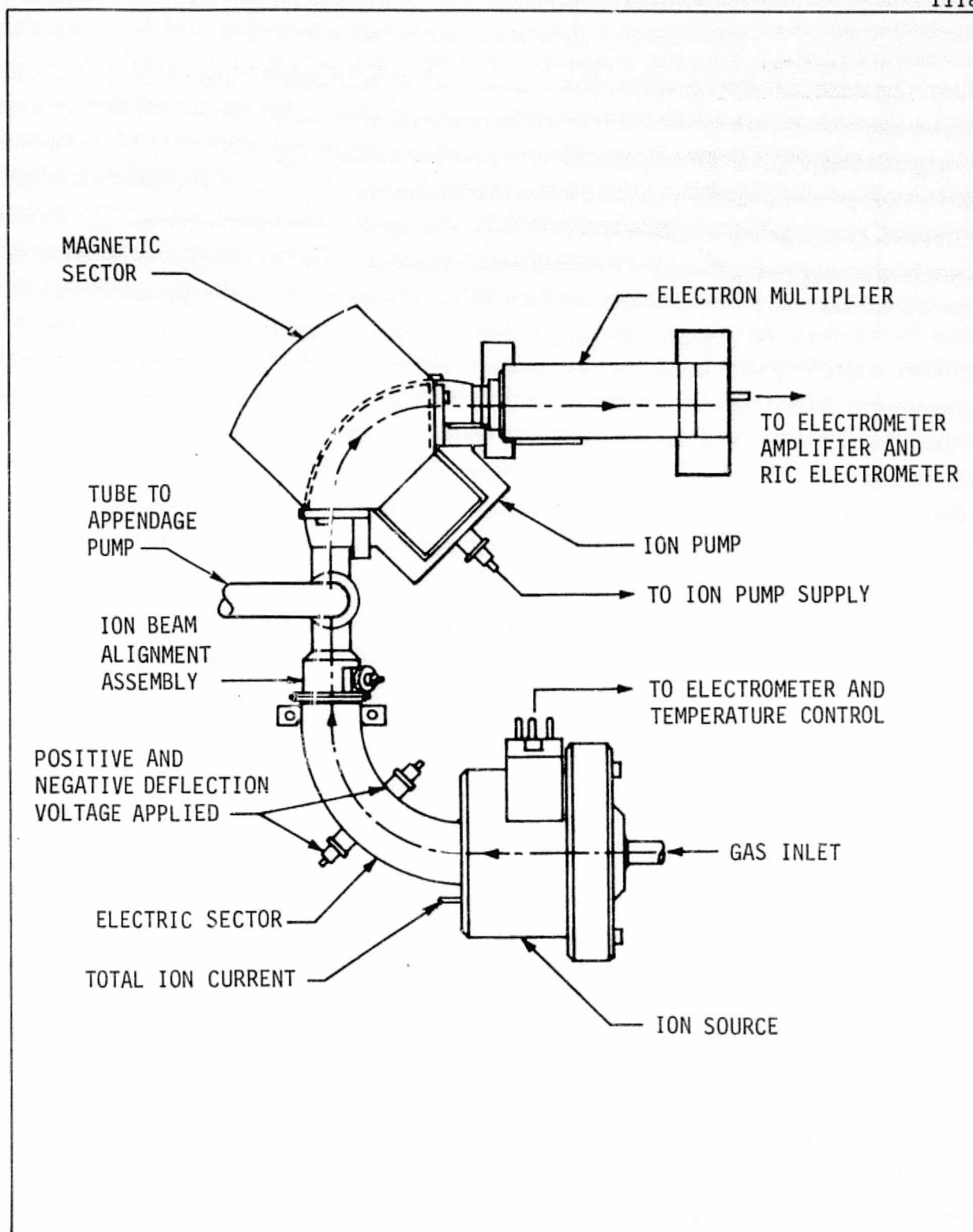


Figure 7-1. Outline Drawing of Mass Spectrometer Analyzer

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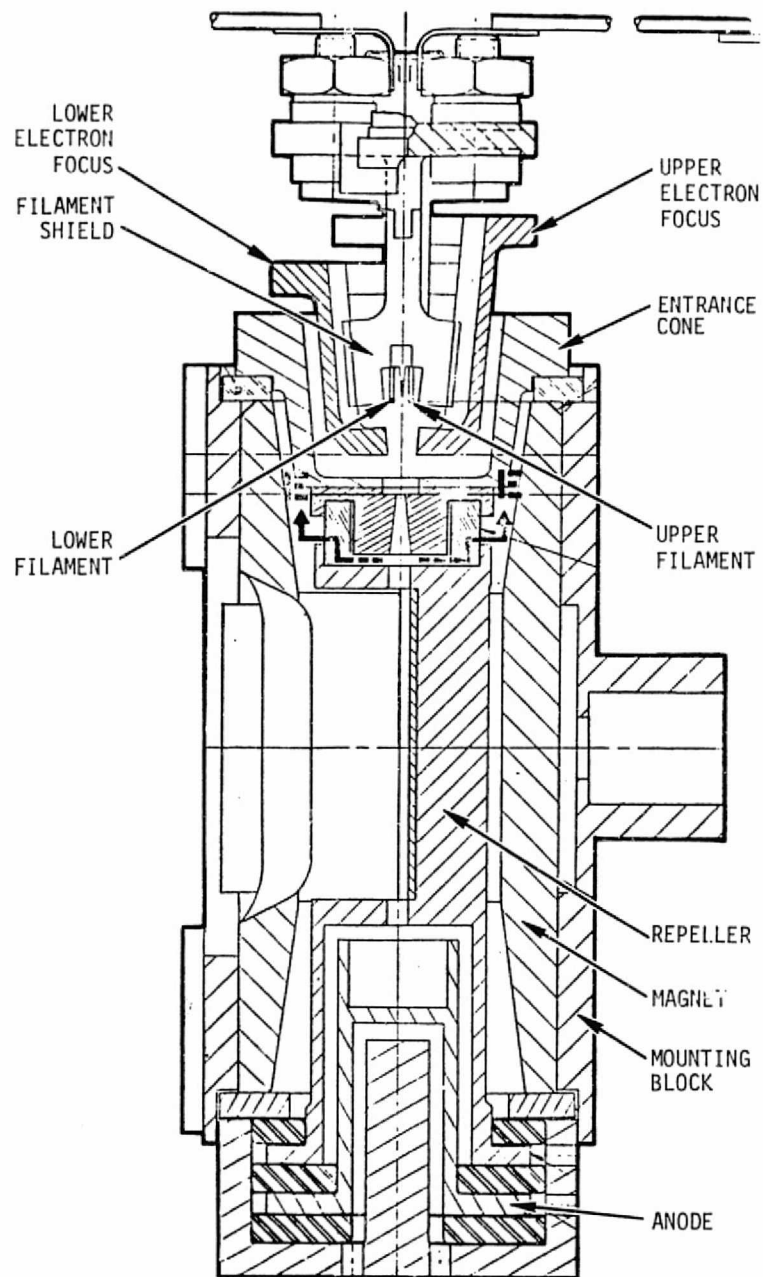


Figure 7-2. Dual Filament Block Assembly

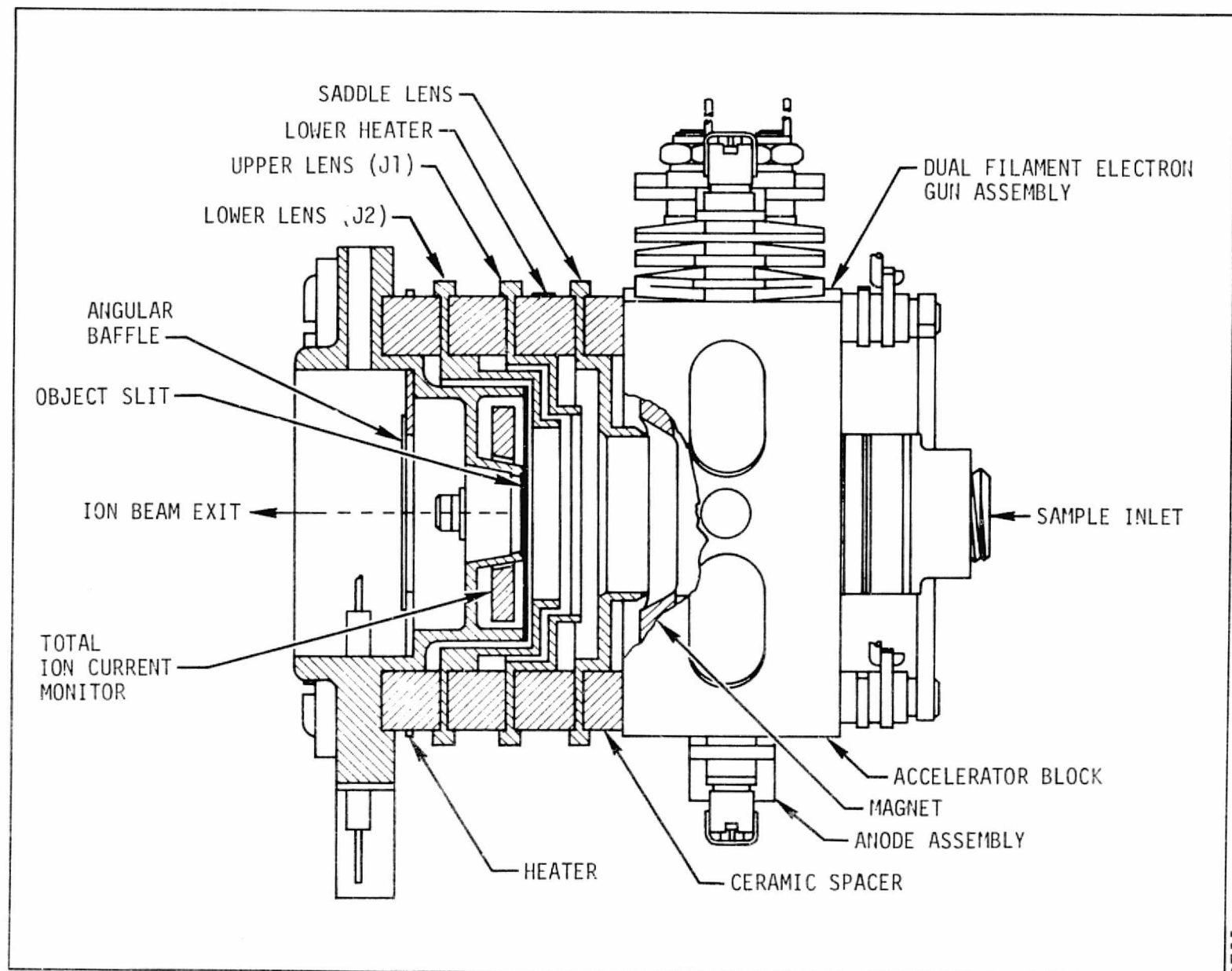


Figure 7-3. Ion Source Assembly (Side View)

Ions formed by electron bombardment are extracted from the ionizing region by the field between the repeller and the source magnet (which is at the mounting block potential). This potential difference is typically 20 volts and forms a strong electrostatic field for ion extraction. This is important to minimize ion space charge effects and increase the pressure range at which the ion source remains linear with total pressure. Since the ions are not formed right at the repeller, there is a constant offset potential applied to the repeller, relative to the scan voltage, to overcome this offset and to allow tracking of the electric sector. A saddle lens is also placed between the mounting block and the split lens to neutralize the offset from the extraction potential and also to block the leakage field from the split lens into the ionizing region. This further improves tracking of the electric sector.

The ions are accelerated through the split lens (J_1 and J_2) to the object slit. A voltage differential is applied to the split lens to correct for any misalignment with the object slit. The object slit has a width of 0.051 mm (0.002 in.) and a length of 0.191 mm (0.075 in.). An angle limiting baffle (the alpha stop) is located between the object slit and the electrostatic sector to limit the beam angular deviations to 1.5 degrees.

The mounting block and ion focusing electrodes are spaced with ceramic ring insulators. They allow the ion source to be sealed to achieve low conductance while electrically isolating the electrical elements which are operated at high potential at the low mass end of the scan (2640 V for m/e 12). The ceramic that isolates the lower split lens from the source base has a deposited nickel-chromium heater element that maintains the ion source at a temperature of approximately 210°C. At the bottom of the ion source is the object slit and total ion current monitor (TICM). The TICM is a ring-shaped collector that surrounds the object slit and collects that part of the ion current that extends beyond the length of the object slit.

A photograph of a closed-heated ion source is shown in FIGURE 7-4.

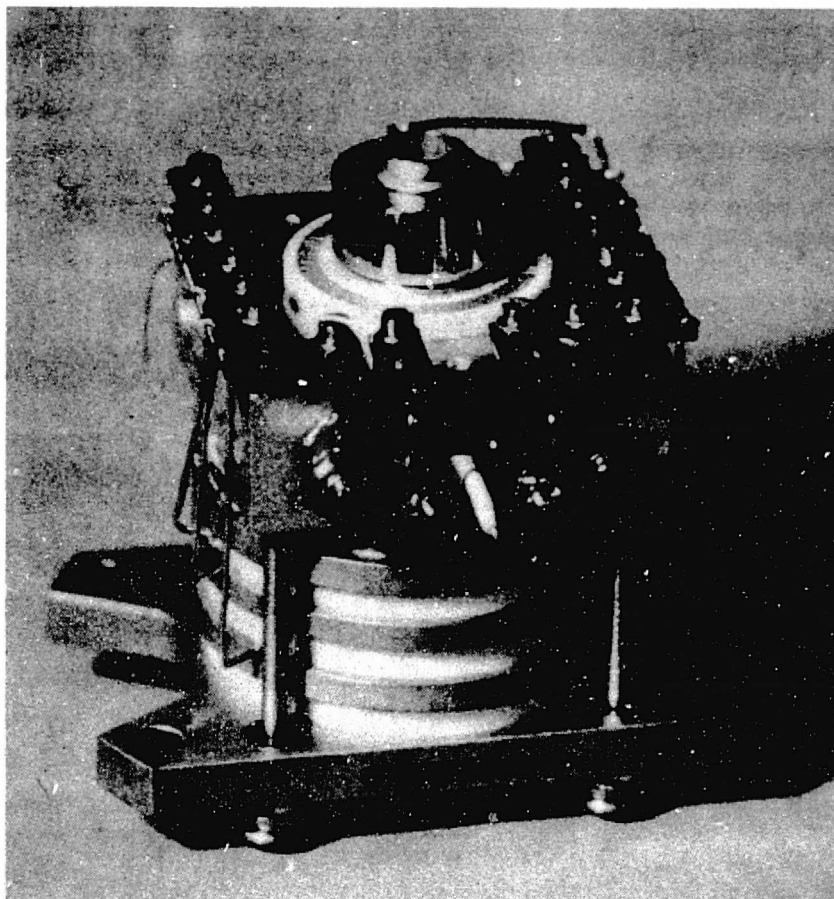


Figure 7-4. Closed/Heated Ion Source

7.2.1.2 The Analyzer

The analyzer housing or vacuum envelope consists of several distinct sections. These include the ion source end cap, the ion source housing, the electrostatic sector housing, the drift tube assembly, the magnetic sector including the ion pump housing, and the electron multiplier housing. The ion source and cap are mounted to the ion source housing with a gold gasket seal and removable clamp flange. The end cap contains the sample inlet tube. The ion source housing contains a 23-pin feedthrough that passes the ion source voltages through the vacuum envelope to the ion source. This header is capable of handling voltages in excess of 3000 volts without breakdown. The ion source housing also contains a single pin feedthrough for the total ion current monitor output.

Following the ion source housing is the electrostatic sector housing. This unit is an extremely rugged section that houses the positive and negative electrostatic sector plates. These electrodes are mounted on many ruby washers and located with ruby dowels to maintain the precise alignment. This assembly is welded to the ion source housing during the assembly process. The electric sector assembly is shown in FIGURE 7-5 and the ion source housing and electric sector subassembly in FIGURE 7-6.

Velocity aberrations in the ion beam are compensated in the 4.577-cm (1.802-in.) radius, 90-degree electric sector. The electroc sector has an aspect ratio of three. This is the ratio of the height of the electric sector to the gap between them. There are Rose shims on the ends of the sector plate to provide field uniformity. A Herzog shunt is used to minimize edge effects at each end of the sector.

The electrostatic sector is followed by the drift tube assembly. A beam alignment slit in the drift tube facilitates adjustment of the repeller potential and sector voltages to obtain an energy focus. It also forms an energy spread limiting baffle. This baffle can also act like a lens to provide Z-axis focusing and improved resolution and sensitivity. The drift tube also contains the pinch-off tube assembly. During test the instrument is attached to an auxiliary vacuum system through the pinch-off tube for the purpose of initial pump down and back-up pump capability to minimize the aging of the flight ion

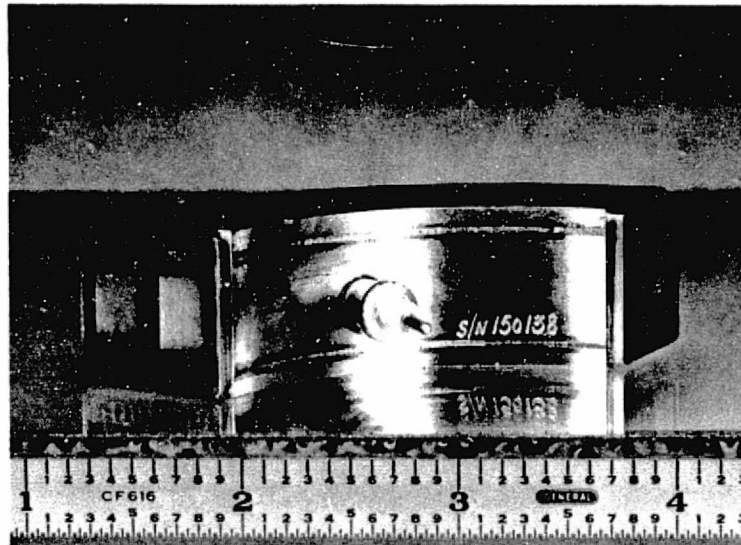


Figure 7-5. Electronic Sector Subassembly

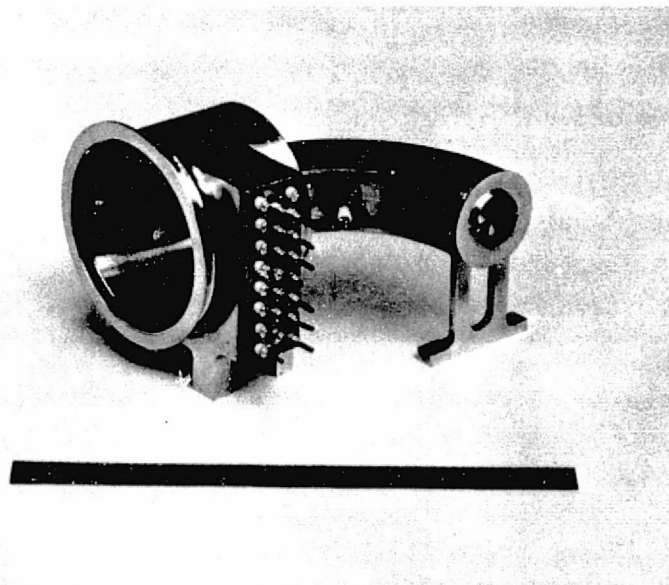


Figure 7-6. Ion Source Housing and Electric Sector Subassembly

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pump during test. A 2-liter/second ion pump is attached at a later phase of system assembly to provide vacuum support.

Mass dispersion occurs in the magnetic sector. As the beam energy is scanned, ions of different mass-to-charge ratio are focused at the image slit plane. The image is corrected to first order in angular and velocity aberrations and to second order in angular aberrations. The 90-degree sector has a 3.81-cm (1.5-in.) radius and a height of 0.254 cm (0.100 in.) in the magnet gap. Pole pieces are welded in the vacuum envelope thereby minimizing the magnet gap magnet weight. Even though the pole pieces are fixed, the magnet itself can be moved to obtain some focusing. An Alnico V-7 magnet provides a field strength of approximately 6300 gauss. A baffle is placed at the leading edge of the magnet sector to limit the number of ions striking the surfaces of the magnetic pole pieces, thereby reducing surface contamination in this critical area. An ion-scattering baffle is placed at the exit from the magnetic sector to prevent ions scattered from the outer radius magnetic sector housing from entering the ion detection electronics. The baffle slit is 1.461 mm (0.0575 in.) in width and is located 1.5 cm (0.6 in.) from the existing magnet boundary. All critical surfaces in the ion source, electrostatic sector, and magnetic sector are gold plated to reduce potential contamination effects.

7.2.1.3 Ion Detection

The ions exiting from the magnetic sector are focused at the image slit. The position of this exit aperture is located in test. An electron multiplier tube is located behind the image slit. This multiplier is a 12-dynode box and grid device utilizing copper-beryllium dynodes. These units are manufactured by ITT to carefully controlled specifications. The dynodes are specially treated to optimize the trade-off between gain and memory effects. The EMT typically has a memory effect which results from electrons that are emitted from the dynodes after excitation is removed. This effect, known as non-self-sustained Mauter emission, can lead to significant peak broadening if the dynode surfaces are not properly controlled. While the EMT can be operated at gains up to 10^6 , this is much higher than the system design requires; a gain of 4300 was utilized in the TGA breadboard system. The EMT is mounted in its own detachable housing with a 6 pin feedthrough to provide the necessary inputs and outputs.

7.2.1.4 Ion Pumps

An ion pump with a nominal speed of 0.5 liter per second is located on the inside radius of the magnetic sector. The pole pieces for the magnetic sector extend over the pump to provide the field required for the pump. The 2.54-cm (1-inch) square titanium cathodes are slotted to provide surface area for noble gas pumping. The anode is stainless steel and consists of an array of 16 equal spaced holes, 5.893-mm (0.232-inch) diameter, drilled through the 2.54-cm by .305-cm (1-inch by 0.12-inch) plate. The flux density required for operation is 2030 gauss. This pump is adequate to handle the gas load required by the analyzer. The magnetic sector assembly and ion pump element are shown in FIGURE 7-7. Additional pump capability for TGA is provided by a 2-liter/s ion pump attached to the drift tube.

7.2.1.5 Sample Inlet

The sample inlet system consists of two sample inlet tubes. One valve is a Parker-Hannifin type for interfacing with the GC subsystem, and the other is a special low-volume valve with a vespel seal for introduction of calibration gases directly to the MS. The use of the hydrogen separator eliminates the need for any type of sample inlet restriction to limit the sample gas flow rate or carrier gas influx. Both sample inlet valves are mounted in close proximity to the ion source end cap to minimize the time constant associated with the sample transport from the output of the separator to the ion source.

7.2.1.6 Mounting

The analyzer is mounted on a 0.95-cm (3/8-inch) thick stainless-steel plate to provide additional rigidity to the analyzer housing. This, in turn, is mounted on the sensor tray, to which the GC subsystem is also attached. On the underside of the tray, the MS electronics are also located.

7.2.2 Performance Parameters for the Analyzer

The performance parameters for the TGA mass spectrometer were characterized in part by tests conducted on the MS prior to shipment. These tests are described in some detail in Appendix III. Results obtained in these tests are not

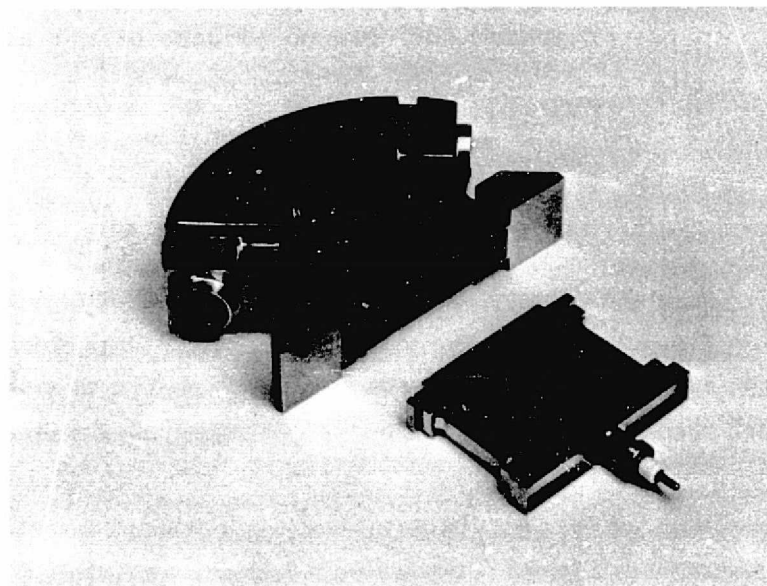


Figure 7-7. Magnetic Sector and Ion Pump Element

strictly comparable to the projected performance because of certain deficiencies in the electronics and because of the limited time available to complete the tests. Nevertheless, the data are sufficient to permit an assessment of the performance of the mass spectrometer relative to the required performance for trace gas analysis.

7.2.2.1 Sensitivity

One of the standard tests conducted on each analyzer is the measurement of nitrogen partial-pressure sensitivity. The value achieved depended on several instrument parameters including filament position and tuning compromises required in order to reduce mass discrimination to achieve acceptable high mass sensitivity. The value used in the system performance analysis was 1.5×10^{-6} ion ampere/kPa (2×10^{-6} ion ampere/torr) source nitrogen. The measured value for the mass spectrometer subsystem was identical to this value. The system sensitivity for nitrogen, mass discrimination, and scan rates establishes the overall instrument capability for detection of contaminants and quantitative determination, as they elute from the GC column.

7.2.2.2 Mass Discrimination

Mass discrimination is just as important a parameter as nitrogen sensitivity because together they establish the sensitivity of the unit at other mass-to-charge ratios. The analyzer was tested for mass discrimination by measuring the ratio of the m/e 31 to the m/e 181 peak for perfluorobutene-2 (PFB-2). Typical values observed when the instrument was properly tuned were 3:1 to 5:1. This ratio, in itself, says nothing directly about mass discrimination because the ionization fragmentation pattern is a strong determiner of peak ratios. The ratio, however, can be utilized to make comparisons between instruments.

The instrument can be tuned to optimize sensitivity for higher mass ions at some trade-off in sensitivity for lower mass ions. For trace gas analysis, it is desirable to optimize sensitivity for ions in the mass range around m/e 100 since this provides better capability for detection of many of the contaminants. This was shown experimentally to be equivalent to optimizing the ratio of ion

currents at m/e 181 to m/e 31 in the perfluorobutene-2 spectra. Using this approach, a value of 0.43 was obtained for the TGA analyzer for the m/e 181 to m/e 31 ratio. Typical values for Viking instruments are lower--0.2 to 0.33. In part this improvement may be ascribed to the higher MV product used in the TGA Analyzer.

7.2.2.3 Resolution

The resolution of the analyzer was measured at three points: (a) the 5% peak height resolving power at m/e 28, (b) the equivalent valley at the m/e 181 peak for two theoretically equal sized peaks one mass unit apart, and (c) the same measurement as the preceding one, but at m/e 200. At m/e 28 typical resolving power values are around 275. At higher m/e values the resolving power is lower because the energy aberration (i.e., due to $\Delta V_1/V_1$) is larger at lower scan voltage. A 10% valley at m/e 200 is probably more realistic for the TGA breadboard. Calculations based on this value and peak shape would project a 22% valley at m/e 250.

The values discussed refer to the unfiltered output of the analyzer. The data that substantiate these numbers were taken using slow scan modes during analyzer test, in which case the effects of filter broadening due to the output filter were not significant. The system calculations were based on a filter characteristic which has a Gaussian impulse response with a half-peak height width equal to one-fifth of the MS output peak width. While this may not be an optimum value, it is consistent with the other calculations on which the anticipated breadboard system performance is based. This type of filter will increase the peak width by the root sum square of the two peak widths or by about 2%. This will increase the anticipated valley at m/e 250 from 22% to 24% based on a Gaussian peak shape extrapolation. A more conservative estimate for the filtered output would be 30% valley at m/e 250 on the filtered MS peaks.

7.2.2.4 Mass Range

The Viking MS subsystem allows the automatic mass scan to cover a selectable range from m/e 25 to m/e 250. This range has been selected because it is

consistent with system performance goals without requiring significant modification to the existing scan supply. With this supply and an MV product of 31,700, the mass range from m/e 12 to m/e 280 can be manually scanned in the TGA system.

7.2.2.5 Gas Flow Considerations

There are several parameters associated with sample gas flow considerations that should be discussed. The GC subsystem including the effluent divider is designed to limit the maximum sample gas flow rate into the analyzer to 1×10^{-6} std-ml/s. This value has been selected based upon an ion source conductance of 40 ml/s for N_2 (at $210^\circ C$) and the decision to limit the maximum ion source pressure to 27 mPa (2×10^{-5} torr). This maximum pressure is a conservative value based upon pressure linearity considerations. There is considerable latitude in the analyzer in terms of accommodating higher flow but this value is consistent with the dynamic range requirements. The integral ion pump itself is capable of sustained pumping at 13 Pa (10^{-2} torr). At this pressure its pumping speed will fall from its nominal value of 0.5 l/s to about 0.1 l/s so the gas load at this point would be 1.3×10^{-3} std ml/s (1 torr std ml/s) which is more than three decades higher than the design maximum. Thus, the existing ion pump is able to handle severe overload conditions without fear of loss of vacuum. From an operational point of view a reasonable upper limit for the ion source pressure is 0.27 Pa (2×10^{-4} torr) or a pump pressure of 2.1 mPa (1.6×10^{-6} torr) (at full pumping speed). At this pressure there would be significant nonlinearity in the output of the mass spectrometer on the high mass peaks but useful mass spectral information would still be obtained over much of the spectrum. Therefore, in terms of over-range capability the existing analyzer will have a margin of one decade in input flow, and in terms of a more serious overload condition it has a margin of three decades in input flow.

The estimated ion source time constant will be 0.2 second for N_2 . The time constants for other compounds will depend upon their molecular weights and chemical properties but should not exceed 1.5 seconds for any compound on the specified list. The differential pumping ratio, that is the ratio of the ion source

pressure to the ion pump pressure, will be 18:1, thus providing a high degree of pump isolation.

7.2.2.6 Stability

No long-term stability testing was run on the TGA breadboard MS subsystem. From previous testing on the Viking MS and on an MS built for Skylab, an 8-hour stability within $\pm 5\%$ is anticipated. Optimistically it might be possible to expect a value as low as within $\pm 2.5\%$ based on the scan-to-scan variation data that was taken on Viking which showed very little change. It is only reasonable to apply these specifications to signal levels for which the signal-to-noise ratio makes the effects of noise on the data small compared to the required stability.

7.2.2.7 Other Factors

The existing analyzer has dual-filament capability as provided for in the Viking design. The properties of these filaments are not presently normalized as would be desirable for an automatic change of filaments in flight in the event of a filament failure. The primary source of this limitation is the compromise tuning potentials required by the existing Viking analyzer electronics. In the TGA breadboard system, the instrument was optimized for performance on one filament. No attempt was made to adjust performance for both filaments.

Filament life should be adequate for the intended mission profile. Perkin-Elmer has operated filaments of this size and material at 2.7 mPa (2×10^{-6} torr) of air for periods in excess of 4000 hours. Hydrocarbons can cause more stringent effects but during a normal mission profile the average pressure level would be extremely low. Experimental data from the Viking program has established the reliability of the present 0.076-mm (0.003-inch) diameter filament design.

7.3 MS Subsystem Electronics

The MS subsystem electronics (FIGURE 7-8) consist of the control and monitor electronics, MS analyzer electronics, and the data conversion electronics.

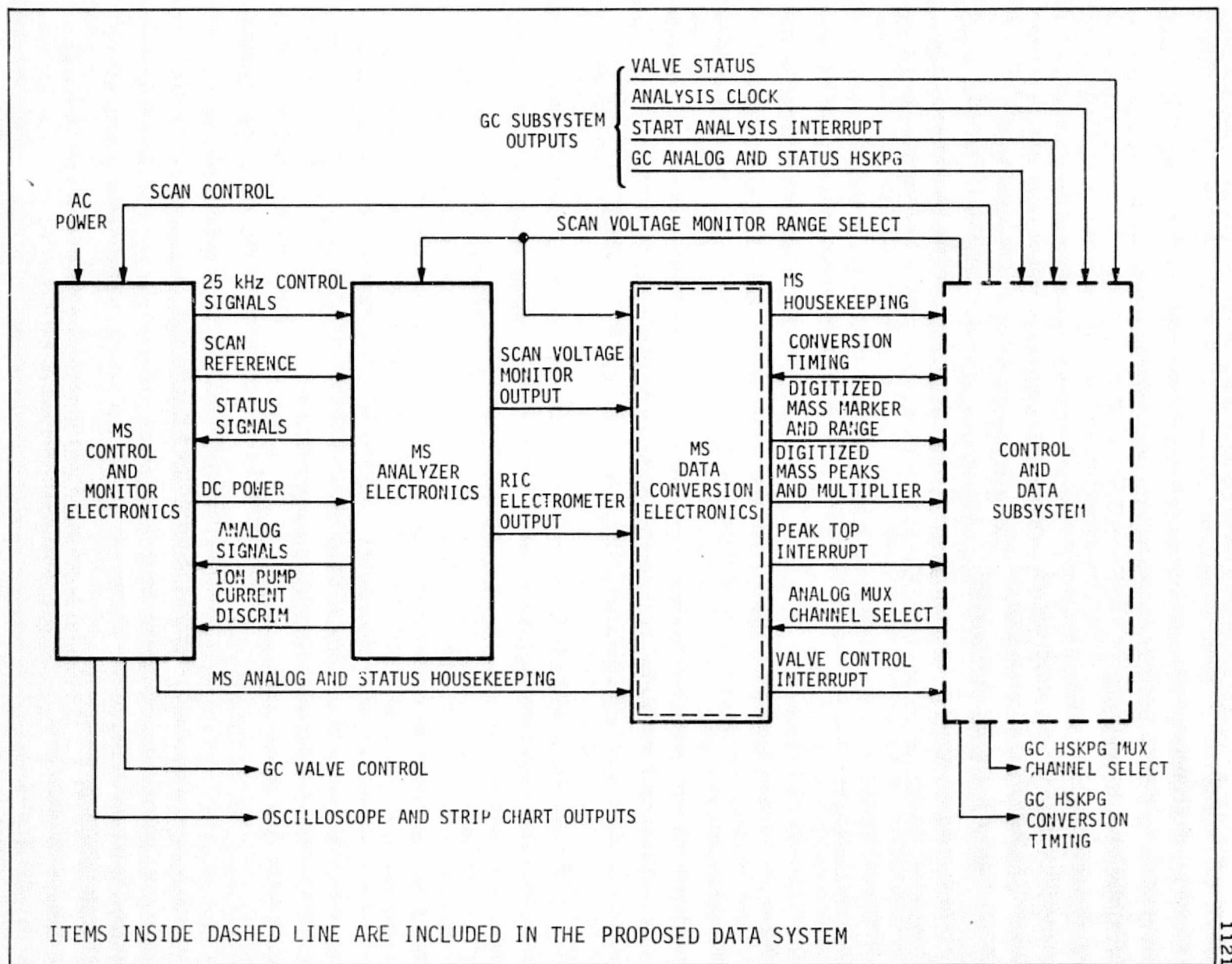


Figure 7-8. Mass Spectrometer Subsystem Electronics

7.3.1 Block Diagram and Description

The control and monitor electronics supply low voltage operating power and control clock signals to the MS analyzer electronics, and serve as a control and monitoring panel for all critical MS analyzer parameters. The MS analyzer electronics include all of the circuits the MS uses to ionize, accelerate, separate, and detect the sample ions and to maintain analyzer vacuum.

7.3.2 Control and Monitor Electronics

The control and monitor electronics are shown in FIGURE 7-9 and the control panel is shown in FIGURE 7-10. These circuits provide convenient control and monitoring of the MS analyzer operation during breadboard testing.

The clock oscillator and countdown circuits develop a 25-kHz clock command signal which enables the MS analyzer power supplies by means of toggle switches. The clock signal and switches allow individual on/off control of the ion pump power supply, ion source temperature controller, and the dc/ac converter which drives the remainder of the MS analyzer power supplies. An additional switch provides the clock command for manual selection of the ion source filament.

The low voltage dc power supplies for operation of the MS analyzer circuits are also included in the control and monitor electronics, as are the power control switching circuits which assure the proper power application timing. Mass spectrometer scan range and rate are also controlled by the control and monitor electronics. An exponential scan generator, which may be programmed manually or by remote computer control, serves as the basis of this circuit.

The voltage end points of the scan may be set to cover any selected portion of the instrument mass scanning range, and the scan rate may be adjusted from 2 to 10 seconds per decade. Manual and computer control of the scan cycle and provision for manual voltage adjustment without scanning are also included.

Several of the MS critical analog functions, mass scan voltage and the outputs of the ion pump, resolved ion current, and total ion current electrometers, are

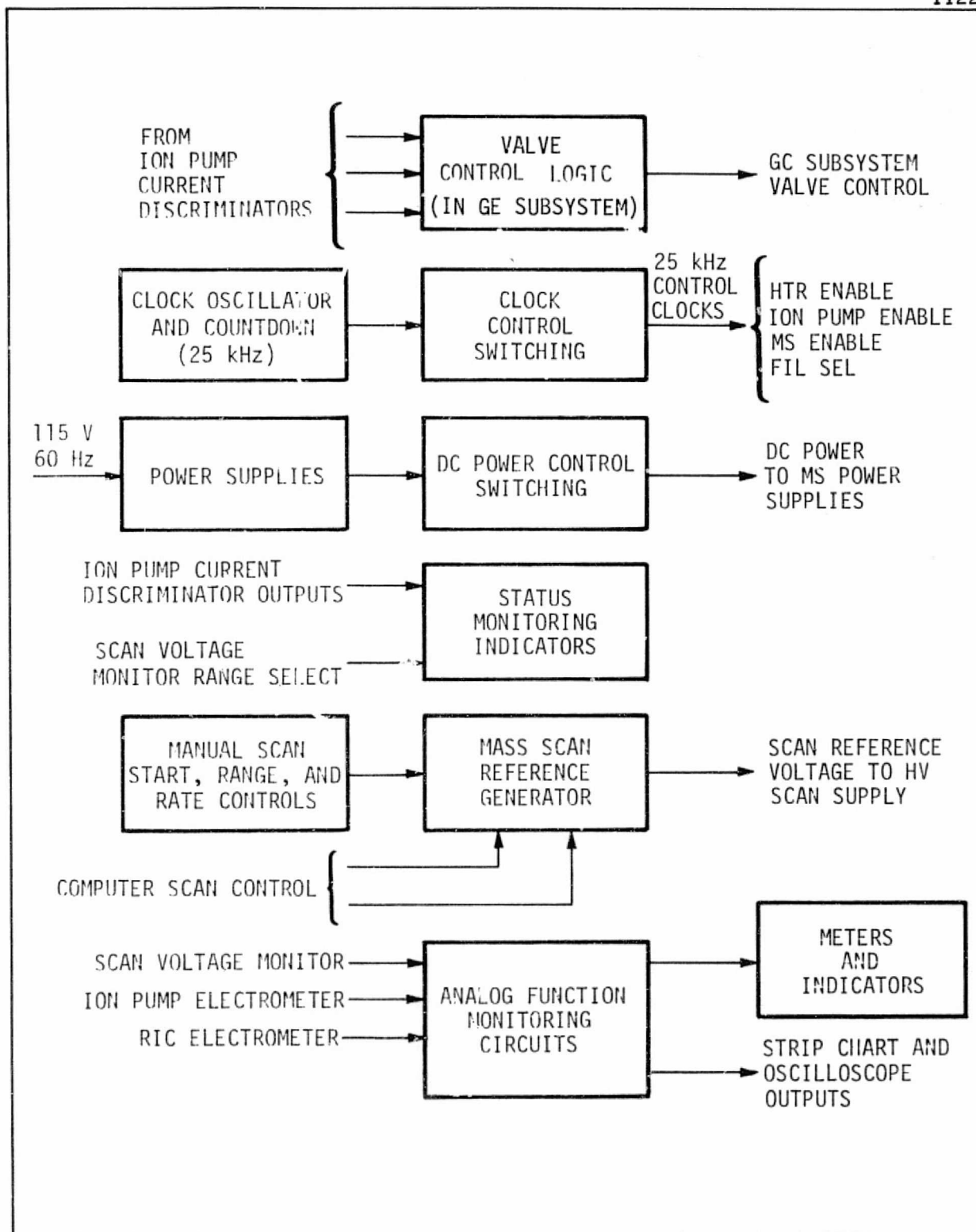


Figure 7-9. MS Control and Monitor Electronics

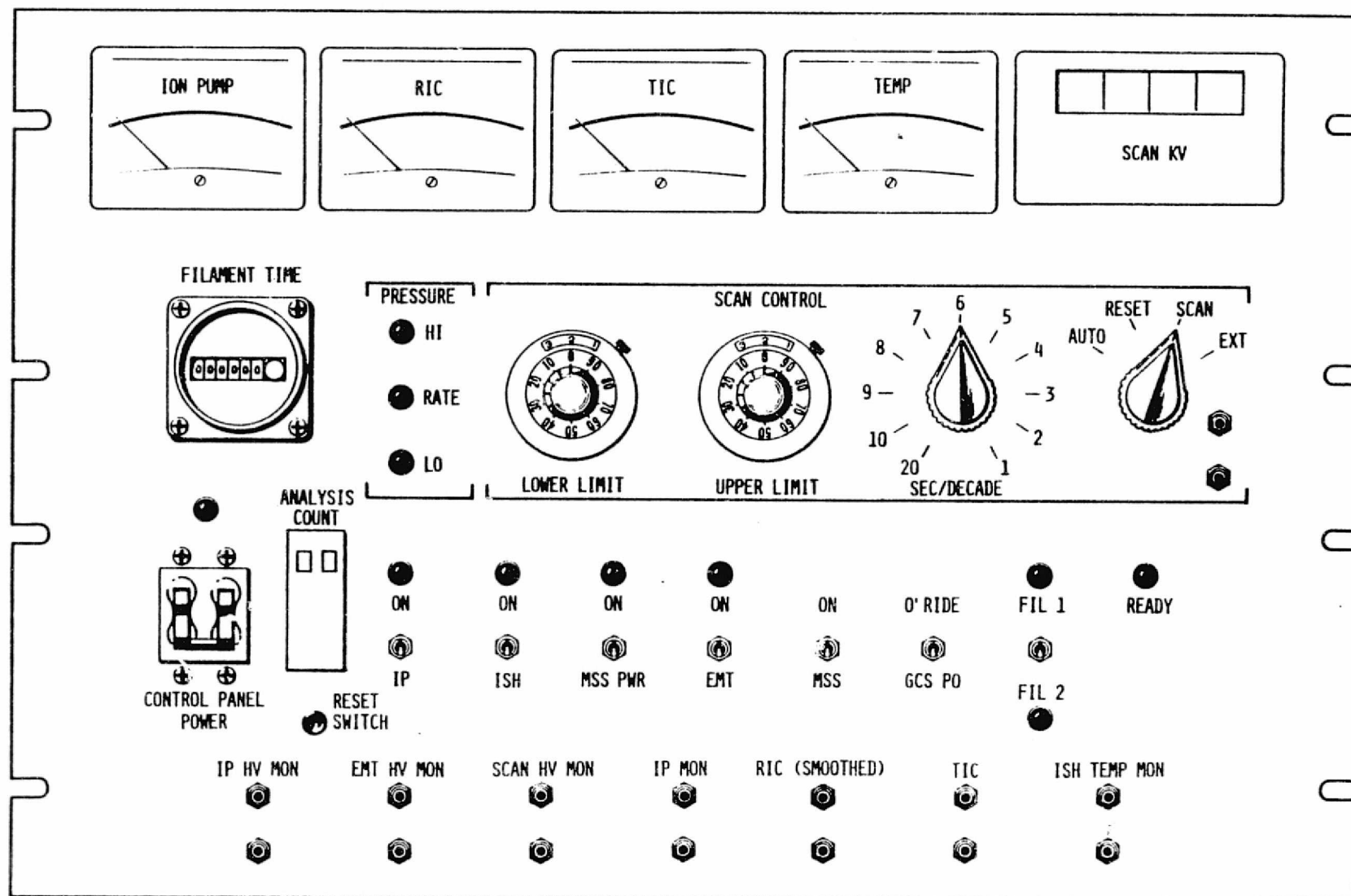


Figure 7-10. MS Control Panel

monitored by meters on the control panel. Jacks are provided for output of these and other critical data and housekeeping analog functions to external monitoring devices such as DVM, oscilloscope, or strip chart recorder. Status indicator lamps monitor switching and sequencing functions.

The control and monitor electronics also provides ion-pump current information to GC subsystem valve control logic, which provides control signals for the effluent division and MS protection valves in the GC subsystem.

7.3.3 Analyzer Electronics

The analyzer electronics (FIGURE 7-11) are essentially those developed for Viking flight hardware, and have been designed for flight applications requiring minimum size, weight, and power consumption. Any redesign required for Shuttle flight hardware should be limited to minor circuit modifications and repackaging, using techniques and processes developed by Perkin-Elmer on the Viking program.

The circuits associated with the MS analyzer include the ion-source temperature controller, ion-source bias supply, emission regulator, EMT supply, ion-pump supply, high-voltage scan supply and dividers, and electrometers for monitoring the ion-pump current and resolved ion current. The analyzer electronics also include discriminators which sense the magnitude and rate of rise of ion-pump current. These discriminators provide logic level outputs which are processed for control of the MS protection valve and the GC effluent divider valves. The output of the high voltage scan supply is sampled by the scan voltage monitor circuit to provide an analog mass marking signal.

Circuit modifications to existing Viking circuits were limited to those required to extend the scan speed and resolution capabilities.

7.3.3.1 Mass Scan Generation

The scan waveform chosen for the breadboard is a continuous exponential decay. The basic waveform is generated in the exponential scan generator portion of the control and monitor electronics and is applied as a reference voltage to

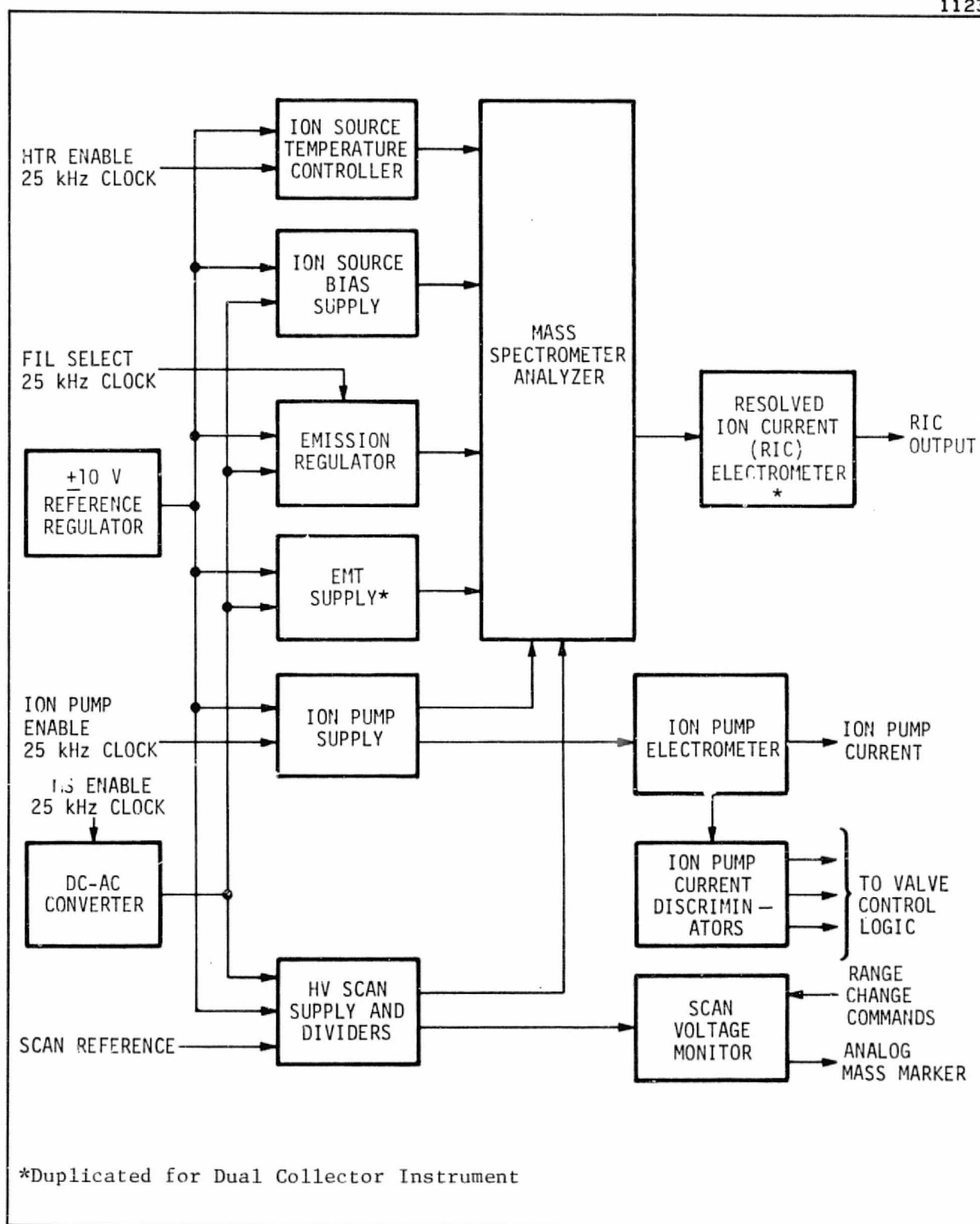


Figure 7-11. Analyzer Electronics

the HV scan power supply. Scan rate adjustment is provided over the range of 1 to 200 seconds per decade, and provisions are included for manual control of upper and lower scan voltage limits.

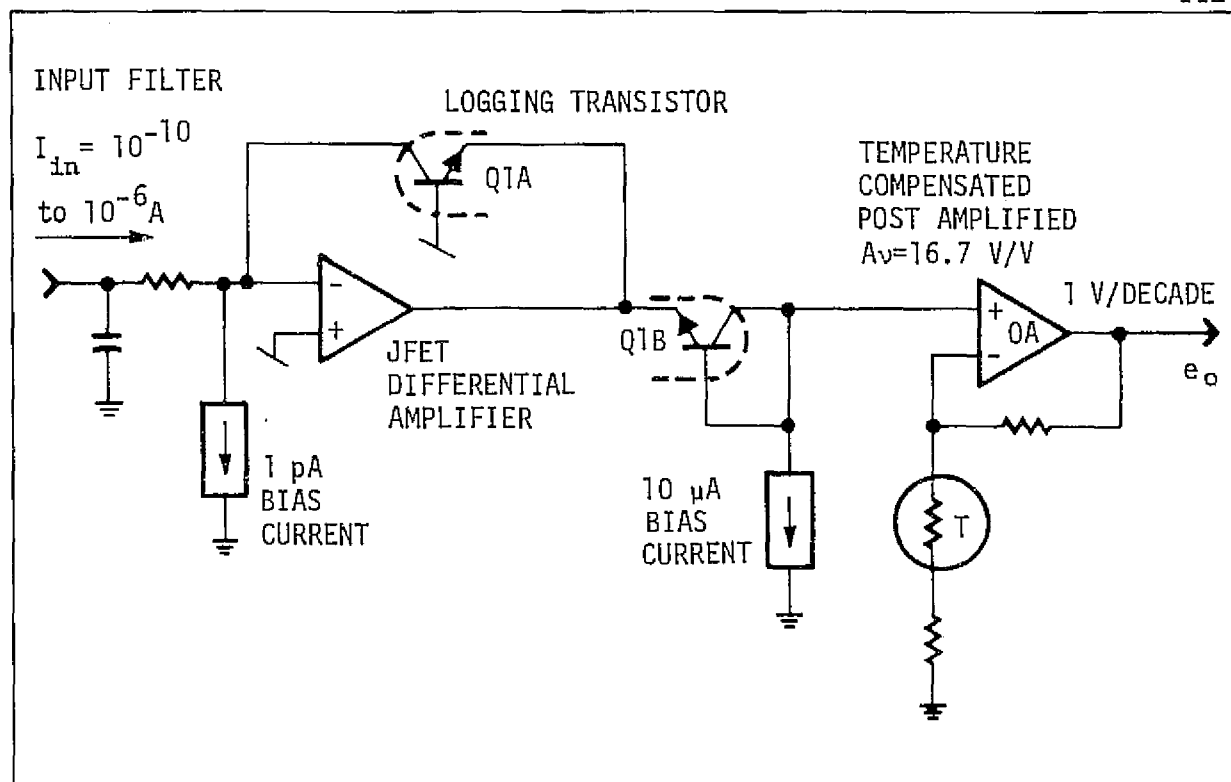
Because the logging transistor (Q1A) parameters are temperature dependent, transistor Q1B is employed to provide cancellation of the effects of leakage currents. In addition, a temperature-dependent resistor is employed in the second stage feedback network to compensate for the temperature dependent term in the transistor transconductance characteristic.

The present Viking high-voltage scan supply circuit is used at these scan speeds, although minor component value changes were made to optimize the tracking of the various outputs.

7.3.3.2 Resolved Ion Current Electrometer

The output signal current from the EMT ranges in amplitude from 10^{-10} A for a minimum detectable peak to 10^{-6} A for a maximum amplitude peak. To accommodate this dynamic range, the nonlinear transfer characteristic of a bipolar transistor is employed in the feedback network to yield an electrometer transfer impedance having a logarithmic gain characteristic. This technique, proven in the Viking mass spectrometer system, provides an output voltage of one-volt-per-decade change in input current.

The electrometer--shown in a simplified schematic diagram, FIGURE 7-12--employs a matched pair of junction field effect transistors (JFETs) for their low leakage current characteristics (10^{-13} A @ 25°C) and excellent voltage noise parameter. At the signal current level of 1×10^{-10} A, the noise contributed by the electrometer is small compared to the noise associated with the ion statistics and EMT. Consequently the overall system performance is relatively independent of the electrometer noise characteristics. In this manner amplitude compression is obtained, thereby permitting low level peaks to be amplified well above the noise level of succeeding stages, yet maintaining the maximum output level within the limits of integrated circuit electronics. To



7-12. Logarithmic Electrometer, Simplified Schematic Diagram

reconstruct the peak data, an inverse log function must then be employed. However, this may be accomplished after A/D conversion to avoid the use of high signal processing circuitry.

Noise introduced in the circuitry following the logarithmic electrometer and prior to A/D conversion introduces constant percentage errors. Consequently, the inaccuracy due to these noise sources affects the high-level signals the same as the low signals. With a linear system the noise components have a diminishing effect on accuracy as the signal level increases. The logarithmic approach trades off accuracy at the high-signal levels in exchange for improved performance at low levels using readily available integrated circuit components.

7.3.3.3 Filtering Considerations

Preliminary design and test of a smoothing filter, A/D converter, and data system electronics were performed in the initial phases of the breadboard program. This effort was terminated due to budgetary and schedule considerations.

8.0 TEST PROGRAM

Because of the modular design of the gas chromatograph subsystem (GCS) and the mass spectrometer subsystem (MSS), each subsystem can be checked independently of the other. The mass spectrometer subsystem with the V7 valve attached is calibrated by introduction of several calibration samples through an auxiliary input valve. The GCS was tested using another Parker-Hannefin valve for the mass spectrometer interface. The valve was connected to a Finnigan Model 750 Mass Spectrometer. The GC subsystem is the sample introduction system and must be tested to demonstrate that it meets functional requirements, whereas the mass spectrometer subsystem is the detector for the system and must be calibrated for various compounds of interest. After each system was independently evaluated, the two subsystems were integrated and tested as a complete system. TABLE 8-1, below, summarizes how the performance requirements for the TGA breadboard were met:

TABLE 8-1 (SHEET 1 of 2). TGA BREADBOARD PERFORMANCE REQUIREMENTS

Sub-system	Requirement	How the Requirement was Met
GCS MSS	Breadboard readily converted to flight configuration.	Many Viking-qualified components in a miniaturized mechanical package.
GCS	Accurate, reliable, reproducible sample introduction into GC.	Temperature-controlled sample valve and sample loops.
GCS	Measure CO.	Provided Molecular Sieve column to separate CO from N ₂ .
GCS	Temperature programming provided if necessary.	Breadboard GFE-GC column can be operated either temperature-programmed or isothermally.

TABLE 8-1 (SHEET 2 OF 2). TGA BREADBOARD PERFORMANCE REQUIREMENTS

Sub-system	Requirement	How the Requirement was Met
GCS	Carrier gas.	H ₂ recirculation system.
GCS	GCMS interface has low weight, size, power, and vacuum requirement.	H ₂ separator. Minimizes system weight, size, power. No additional vacuum requirements.
MSS	Mass spectrometer design (no restriction).	Use Viking double-focusing MS.
MSS	Scans 24-240 amu, uninterrupted.	Scans 24 to 240 amu, single uninterrupted scan.
MSS	Scans any interval between 24-240 amu.	Intervals between 12-240 can be scanned by selecting voltage end points.
MSS	Scan rate variable 2 to 10 s/decade.	Scan rate of 1 s/decade to 200 s/decade manually changeable.
MSS	Maximum 1-s delay between scans.	Provided to input engineering data onto tape.
MSS	Resolution $M/\Delta M = 1$ at 200 amu, with 10% valley.	Resolution $\frac{M}{\Delta M} = 200$ (10% valley) $\frac{M}{\Delta M} = 250$ (30% valley) on the filtered mass peaks.
MSS	Detect 5×10^{-9} gm/s at 2/1 SNR.	MS sensitivity of 49.2×10^{-12} gm/s for N ₂ .
MSS	EMT gain 10^6 .	4800 gain at 1800 V.
MSS	Stability $\pm 0.1\%$ at SNR 10/1 over 8 hr on single peak.	$\pm 5\%$ at SNR 10/1 per scan over 8 hr.
MSS	MS has provisions for oscilloscope monitoring.	Test connectors are provided for attachment of an oscilloscope or oscillographic recorder.
MSS	Optimum longevity filaments.	Dual filament W, 3% Re 0.076 mm (0.003 in.).
MSS	Provide peak retention times to the data subsystem.	Instrument sequencer can feed clock signals to data system.
MSS	Design to eliminate noise.	Breadboard incorporates single-point ground technique and proper shielding.

8.1 GC Subsystem Tests

After assembly was completed, the GC was attached to our Finnigan mass spectrometer for initial testing. A diagram of the test system is shown in FIGURE 8-1. Data that were accumulated during these GC subsystem tests are described in the following paragraphs.

8.1.1 Pressure Control Loop

This test determined whether the pressure control circuit for controlling the pressure upstream of the flow control restrictor was operating normally. To accomplish this test, the T-zone was heated to operating temperature and then hydrogen flow begun. After a period of time needed to establish flow stability, three measurements were made: pressure limits (high and low), cycling time of the upstream valve V2, and separator current stability. Initial tests run with the system had the pressure limits set between 1.393 to 1.396 MPa (202.1 to 202.45 psi). With these close limits it was found that the valve cycled often. A feedback resistor in the circuit was changed so that the pressure was controlled from 1.38 to 1.41 MPa (200 to 204 psi). This was found to be more acceptable so far as valve cycling time was concerned. After the new pressure limits were set, the valve, V2, cycled approximately once every six minutes. Separator current was found to be very stable due to the damping effect of the column and effluent divider. For the next generation system a larger equilibrium volume probably should be used, which will cause less valve cycling and, therefore, less wear on the valve. A larger volume would mean less pressure increase when the GFE column is temperature-programmed, and during shut-down of the system when all the hydrogen is pumped from the lines into the equilibrium volume.

8.1.2 Organic Sample Injections

For some preliminary GC subsystem testing, a septum injector was inserted just upstream of the column for direct sample introduction with a hypodermic syringe. Various concentrations of samples could be introduced in this manner from vapor samples down to samples that are in a range from 10 to 100 ppm. Low concentration samples are obtained from a permeation-tube/oven system. With the slider valve in place, these various compounds can be injected by filling the sample

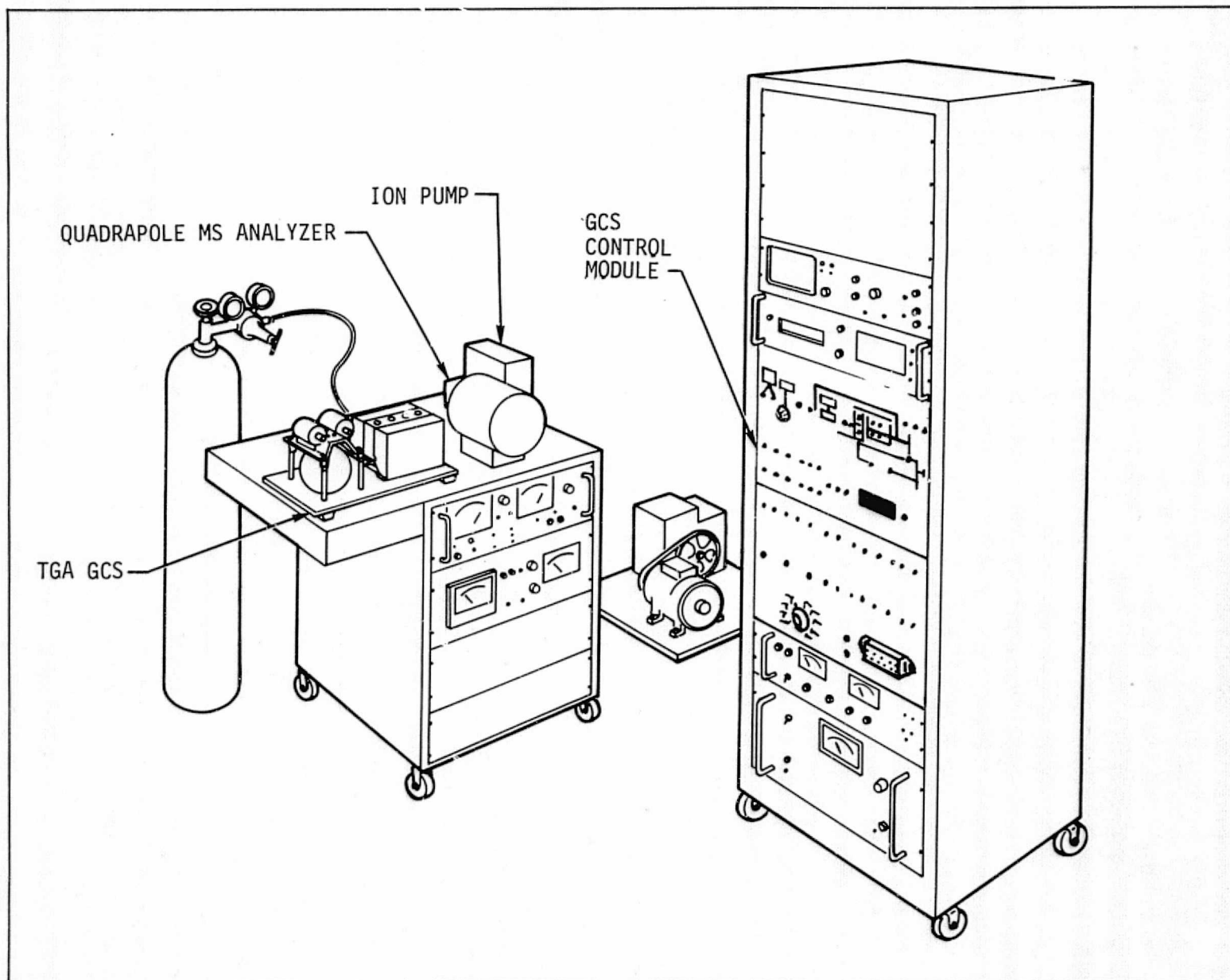


Figure 8-1. GCS/LAB-MS Test Configuration GCS Control Module

loops with the desired sample at any concentration, then switching the slider valve which injects the sample into the GC subsystem. This type of testing will confirm GC peak shape, cold spots in the system, sample transmission, and component elution time. Several compounds were checked on the GC subsystem by septum injection. CO was injected at various levels in ranges of 10 and 100 parts per million. Methanol was also injected in the concentration range of 10 parts per million. This testing was done before the installation of the slider valve. By septum injection, methanol was found to have a peak width at half-height of approximately 30 seconds. After the slider valve was installed, CO, ethyl acetate, and methylethyl ketone, methyl chloroform, carbon tetrachloride, methylene chloride, methyl alcohol, and butyraldehyde were injected into the GC subsystem using a packed column similar to that used on the Viking system. The packed column was used because the capillary organic column was not available at this time. The peak shape of each eluted compound was measured. There was no attempt to scan the spectra during elution to determine whether the eluting compound was the same as the compound that was injected into the system. From the injection of methyl chloroform and carbon tetrachloride, several small peaks eluted. These peaks were probably a result of decomposition of the packed column material because of the solubility of this material in the injected samples.

During GC subsystem testing, permeation tubes were used to obtain small concentrations of various sample components. During this testing, the permeation-tube oven was accidentally overheated causing a butyraldehyde permeation tube to rupture and empty about 2 ml of liquid butyraldehyde into the sample loops. Before this rupture could be detected, a sample was injected into the system by actuation of the slider valve. This sample, as it turns out, was a liquid sample rather than a small vapor sample. The liquid butyraldehyde sample was injected into hot (225°C) connecting lines. Separate tests have shown that butyraldehyde placed on a hot stainless steel plate will polymerize, leaving a residue of white material. This accident with the system possibly resulted in a coating of all the stainless steel connecting lines with a coating of polymerized butyraldehyde. This material on the surface of the tubings could cause sample absorption or peak spreading or tailing. Subsequent methyl alcohol injection

showed that the eluted peak was broader than previous septum injections. The system was baked overnight at maximum operating temperature to vaporize any butyraldehyde that was left on the walls of the system and to carry it out the vent line to the atmosphere.

8.1.3 Hydrogen Separators

Background current of the hydrogen separator is determined during GC subsystem test. The background current of the vent line separator is determined by placing the effluent divider in the 1:1 mode, then waiting a period of time for the current to stabilize at the background level. The background current of the MS separator is determined by placing the effluent divider in the 8000:1 mode, again waiting for the current to stabilize at the background level. This testing will confirm the operation of the separator with the 1.38 MPa (200 psi) back-pressure on its vent line. The efficiency of the MS separator can also be determined by placing the effluent divider in the one-to-one mode and measuring the amount of hydrogen that is transmitted through this separator. The measurement is made by monitoring the signal at mass 2 with the mass spectrometer when V7 is opened, and then closing V7 to get a background reading of the value of mass 2--which corresponds to hydrogen signal. The system hydrogen flow rate can also be determined by measuring the separator current, subtracting the background current of that separator, and dividing the resulting current by 0.143 A per ml. The resulting number is the hydrogen flow in standard ml per minute.

8.1.4 Permeation Tubes

Permeation tubes that were used for obtaining calibration samples for TGA testing are sections of Teflon tubing approximately 6 mm (1/4 inch) in diameter, 150 mm (6 inches) long, and are filled with the appropriate liquid test samples. The diffusion rate of the sample through the walls of the Teflon tube is determined by weighing the tube and then placing it in an oven at a fixed temperature--normally 60°C--for about 24 hours. The tube is then weighed and the weight loss per unit time is the rate at which the sample diffuses through the Teflon tubing. The permeation tube is placed in a fixed temperature oven and a certain amount of purged gas flows around the permeation tube which dilutes the material coming from the permeation tube. By this method, concentrations in a

range of 10 to 100 parts per million are accurately obtained ($\pm 5\%$). These permeation tubes, containing the liquid organic sample, are used for instrument calibration. In the breadboard system, the temperature of the tubular oven that houses the permeation tube is controlled by one of the temperature controllers that was originally designated for line heater control. With this inlet system a gas blend mixture can be used instead of the purged gas for calibration of various gaseous compounds such as 1-butene.

8.1.5 Preliminary Test with Organic Column

Before the organic column was attached to the TGA breadboard system, it was connected to a laboratory test system that included an ultrapure hydrogen supply, a GC oven and an electro-chemical hydrogen separator, and a Finnigan mass spectrometer. This test was conducted to determine whether the column-separator combination was compatible.

The column was first attached to the hydrogen supply and baked overnight at 120°C with 4 ml/m of ultrapure hydrogen flow. The column was then attached to the separator and mass spectrometer and operated for several days at various column temperatures. The results from this test showed much deactivation of the separator when the column was in a temperature range between 50° and 70°C. At temperatures above or below this span, the high efficiency of the separator returned. The reason for this phenomenon was unknown and confusing, but to prevent possible deactivation of the MS separator on the TGA breadboard, the effluent divider was not allowed in the one-to-one mode when running subsequent organic analysis. Later testing of the separator with a Viking column showed that the deactivation of the separator was caused by a temperature fluctuation and not a chemical deactivation of the silver palladium tubing. The conclusion from the testing of the GFE column with the hydrogen separator shows that they are compatible and no permanent degradation of the separator occurs from bleed from the GFE column.

8.1.6 Summary

The GCS testing showed that for every compound injected, at least one peak of some amplitude eluted. The testing with the GC subsystem was conducted using

a 2-meter Viking column. It is noted that the methanol peak--after the system was contaminated with butyraldehyde--was considerably broader than before contamination. The separator efficiency and separator current background were found to be acceptable for use on the breadboard instrument. The pressure control loop with new pressure limits, 14 kPa (+2 psi), is also acceptable for use with the breadboard instrument.

8.2 MS Subsystem Tests

The MS subsystem was completely assembled and tested at Perkin-Elmer before being delivered to Beckman for integration into the TGA breadboard. A summary of the test results is given in TABLE 8-2. Test details are described in Appendix III.

TABLE 8-2. PARAMETERS FOR THE TGA MASS SPECTROMETER

Parameter	RFP	Analysis (Required)	Breadboard Results
Mass Range Automatic Manual	2 to 300 2 to 300	24 to 200 ¹ 12 to 200	24 to 240 12 to 250
Scan Time	2 to 10 s/dec	3 s max for mass range ²	1 to 200 s/dec
Resolution m/dm	300 (10%)	170 (10%)	200 (5%) 200 (10% after degaussing)
Sensitivity, minimum for GC elution	5×10^{-9} g/s SNR = 2/1	2.5×10^{-14} g/s ³	6.2×10^{-10} g/s (worst case CCl ₄)
Source Sensitivity for N ₂	Not specified	N/A	0.012 A/Pa (0.88×10^{-2} A/torr)
Gain	10^6	N/A	4300 gain at 1800 V
Pumping Speed	Not specified	N/A	2 l/s including appendage pump
Stability, 8 hr	$\pm 0.1\%$ at SNR-10	N/A	Est $\pm 5\%$ at SNR of 10/1
¹ Need to monitor m/e 12 during CO analysis ² Assuming GC peaks, 20-s half-width ³ Assuming acrolein at 0.06 mg/m ³ , 0.5-ml sample, and 20-s wide GC peaks			

8.3 System "TGA Breadboard" Tests and Results

The system test consists of two different types of tests--engineering and science. The Engineering Tests are devised to check out the entire system, where the Science Tests are designed to introduce samples of various concentrations into the system to determine how well the system performs. If the system performs as designed, the instrument would be acceptable for use as a trace gas analyzer for space shuttle applications. TABLE 8-3 is a summary of the required Engineering Tests.

TABLE 8-3. REQUIRED TGA ENGINEERING TESTS

Type of Test	Test Method	Data Resulting	Results
System Leak Test	Attach Leak Detector to vent line restrictor and purge instrument with He.	System Leak Rate	$<1 \times 10^{-8}$ std ml/s
Electrical Checkout	Test all electronics to verify instrument's manual operation.	None	All electronic except TIC monitor are functioning normally.
HSA pressure-control loop & recirculation system	Flow 4 std ml/min of H_2 with eff. div. in 1-1 and MS inlet valve open.	Stability of separator and equil. volume pressure and H_2 tank pressure loss.	Pressure control is set at 1.4 kPa (+2 psi) 1% variation in separator current (carrier flow).
Automatic operation of Effluent Divider	Slowly backfill system with N_2 through vent line restrictor.	Pressure level at which semi-automatic eff. div. circuit operates.	MS discriminator levels protect the MS from overpressurization.
Effluent Divider pumpout characteristics	Slowly backfill system to a stable level and switch eff. div. manually to next higher division ratio.	Pumpout time for each restrictor.	Pumpout characteristics are shown in FIGURES 8-2 and 8-3.
Effluent Divider	At a stable system pressure level, switch eff. div. manually to lower division ratio.	Time for stabilization of division ratio.	Repressurization characteristics are shown in FIGURES 8-2 and 8-3.

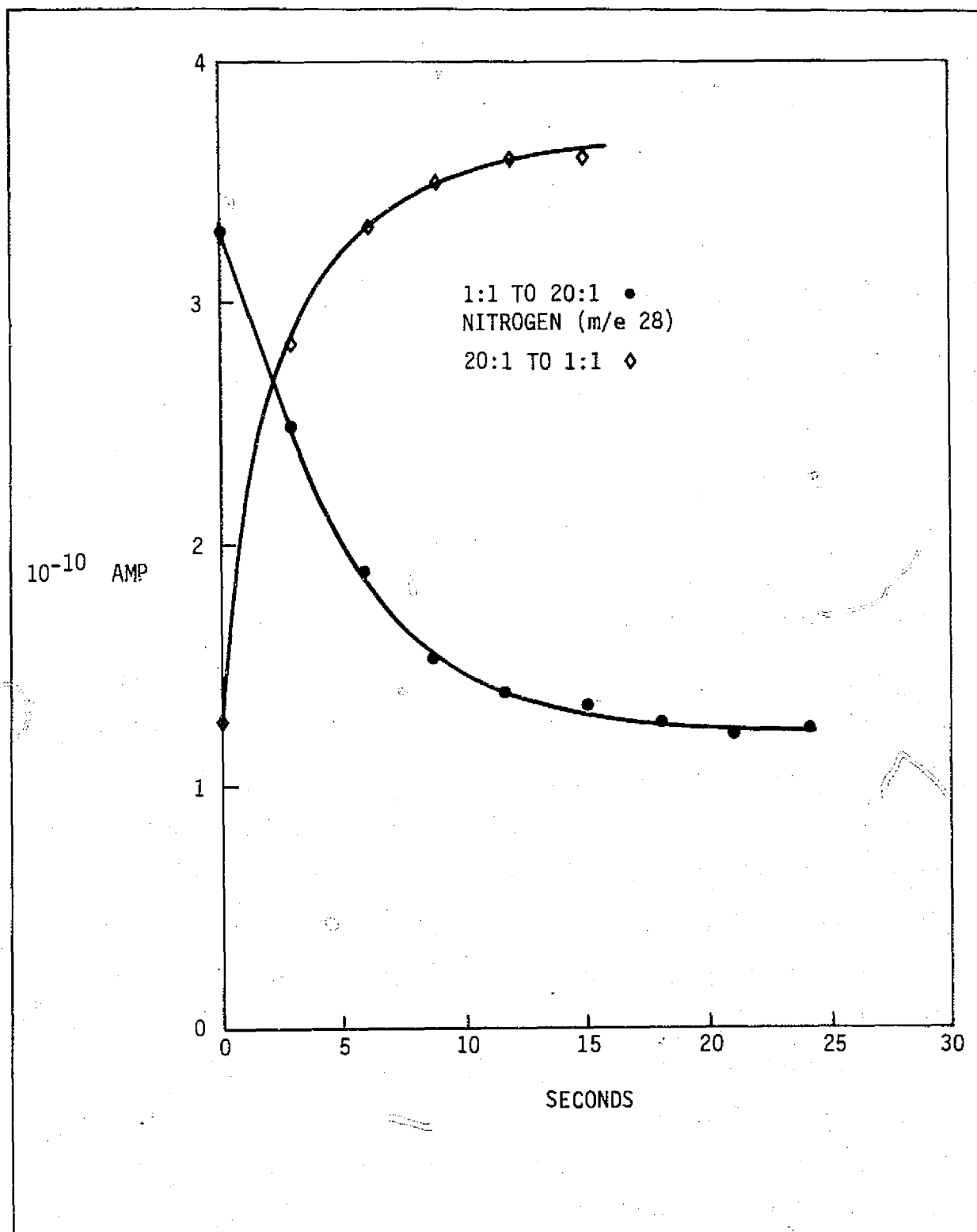


Figure 8-2. System Pumpdown and Repressurization

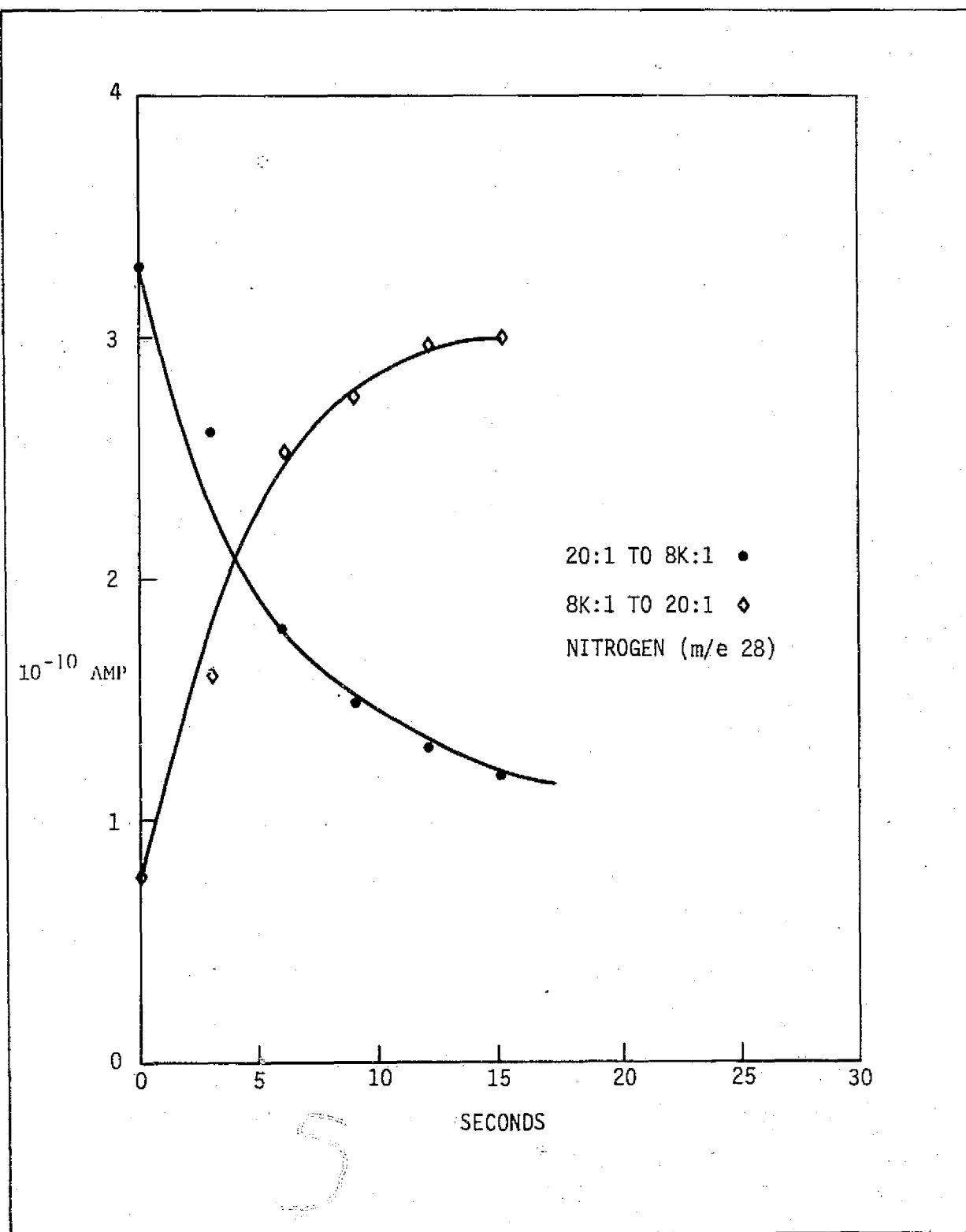


Figure 8-3. System Pumpdown and Repressurization

8.3.1 Effluent Divider Pumpout and Repressurization Test

To determine the response time of the system after the effluent divider was switched, the pumpout or repressurization characteristics were measured by monitoring the nitrogen signal at mass 28. Curves of these pumpouts and repressurization tests were shown in FIGURES 8-2 and 8-3. In general, the pumpout and repressurization time is less than 10 seconds for 90% response going from the 1:1 to the 20:1 mode, or from the 20:1 to the 1:1 mode. This response is fairly slow if the eluted GC peaks are only 10 to 15 seconds wide at half-height. During a GC analysis, it is desirable for the effluent divider not to actuate during the elution of any GC peaks of interest. To meet this requirement consistent with the present dynamic ranges of the system, it would be necessary to vent some of the sample at all times. This would decrease the system sensitivity; however, system sensitivity was found adequate when the effluent divider was in the 20:1 mode (95% of the sample vented). If the effluent divider was left in some split mode--5:1, for example, when no large air samples were eluting--then the effluent divider could be placed in the 5:1 mode sooner on the tail of the eluting water peak or when the GC system background is high. Continuous splitting will allow the elimination of the restrictor in the vent line which will lower the column operating pressure. This pressure decrease has been shown to optimize the peak shape of methanol and will probably optimize the tail of the eluting water peak. The lower column operating pressure will also decrease the elution time of all components, therefore decreasing the analysis time.

8.3.2 Science Test

Science Test Data results directly from the injection of various compounds of interest into the system. The measurement of these compounds over certain periods of time are the main basis for the various science tests. An outline of the science tests that were planned is attached in Appendix I. A summary of the required science tests is shown in TABLE 8-4.

The calibration curves for the various compounds that were injected into the system (methyl ethyl ketone, ethyl acetate, dichlorobenzene, methylene chloride,

TABLE 8-4. REQUIRED TGA SCIENCE TESTS

Type of Test	Test Method	Data Resulting	Results
System Calibration	Inject a test gas sample (<50 ppm) into system and measure response. Use additional classes of compounds at various concentration levels.	MS signal and S/N ratio for various compounds.	Calibration curves (response vs. concentration) are shown in FIGURES 8-4 through 8-9.
System Precision	Inject a selected sample mixture for several instrument cycles daily for several days.	Within-day and day-to-day precision of instrument and test technique.	A summary of intra-daily and inter-daily sampling is displayed in TABLE 8-7.
System Accuracy and Component Transmission Levels	Using sample mixtures characteristic of the various compounds, dilute in flow stream and inject into system.	MS signal for various samples at various concentrations.	Estimated system sensitivity (transmission) level is shown in TABLE 8-6.
Column Performance	Inject a several-component mixture periodically during testing.	Elution time and peak shape.	Compound elution time and peak shape are consistent with the elution of the air peak.
Component Elution Times	Inject various compounds.	Elution time affecting instrument cycle.	CO elutes in 25 min. o-diCl Bz. elutes in 77 min. Total analysis time 102 min.
System Background Vs. Time	Periodically take MS scans with columns cold and hot and with inlet valve closed.	System background vs. system use.	Because the system was operated in the 20:1 split mode, the MS background was consistently below the low trip level.
System Resolution	Compare peak shape and elution time from above tests with data on column.	Compound separation.	Compound elution times are repeatable to within ± 15 s.

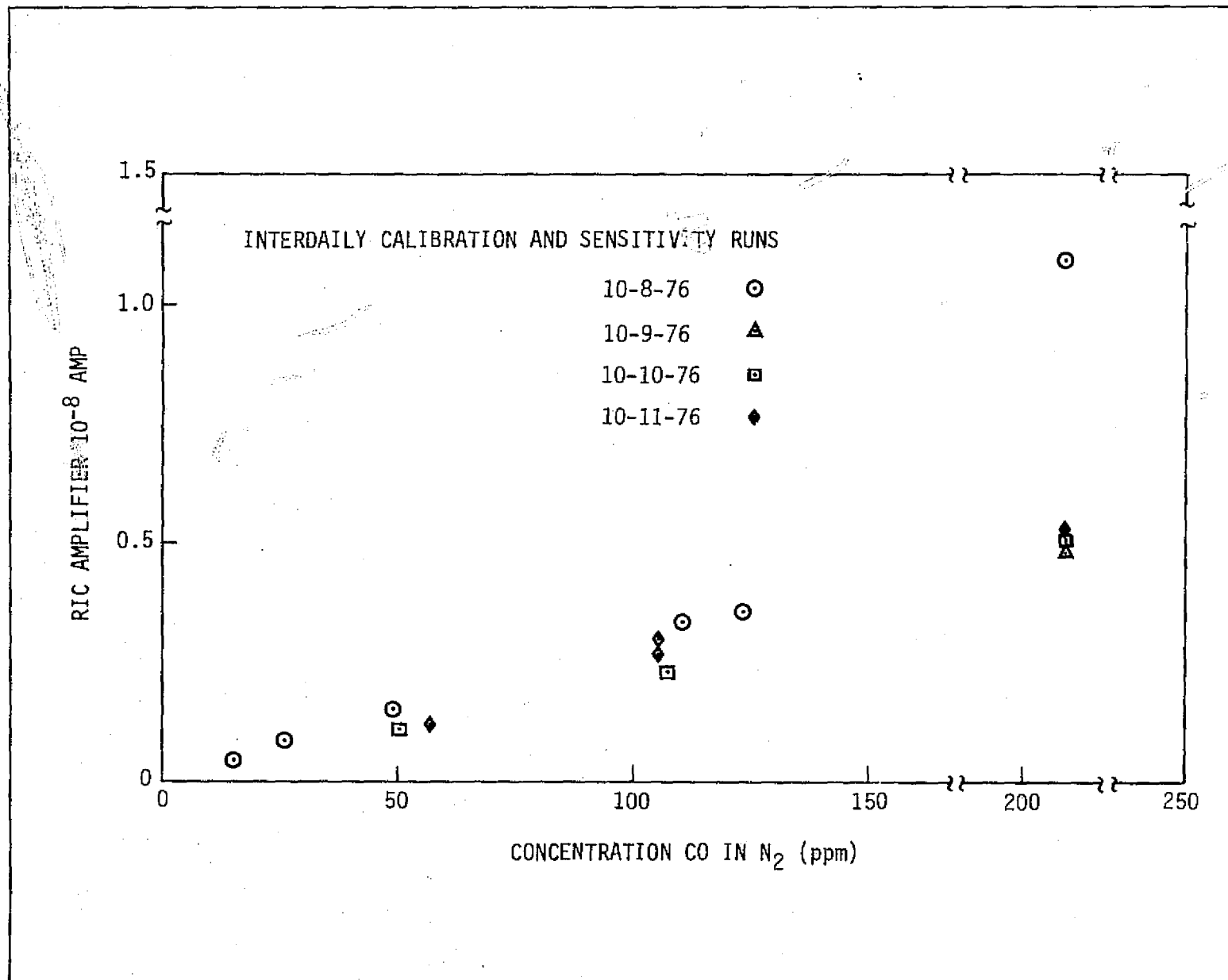


Figure 8-4. Calibration for Carbon Monoxide

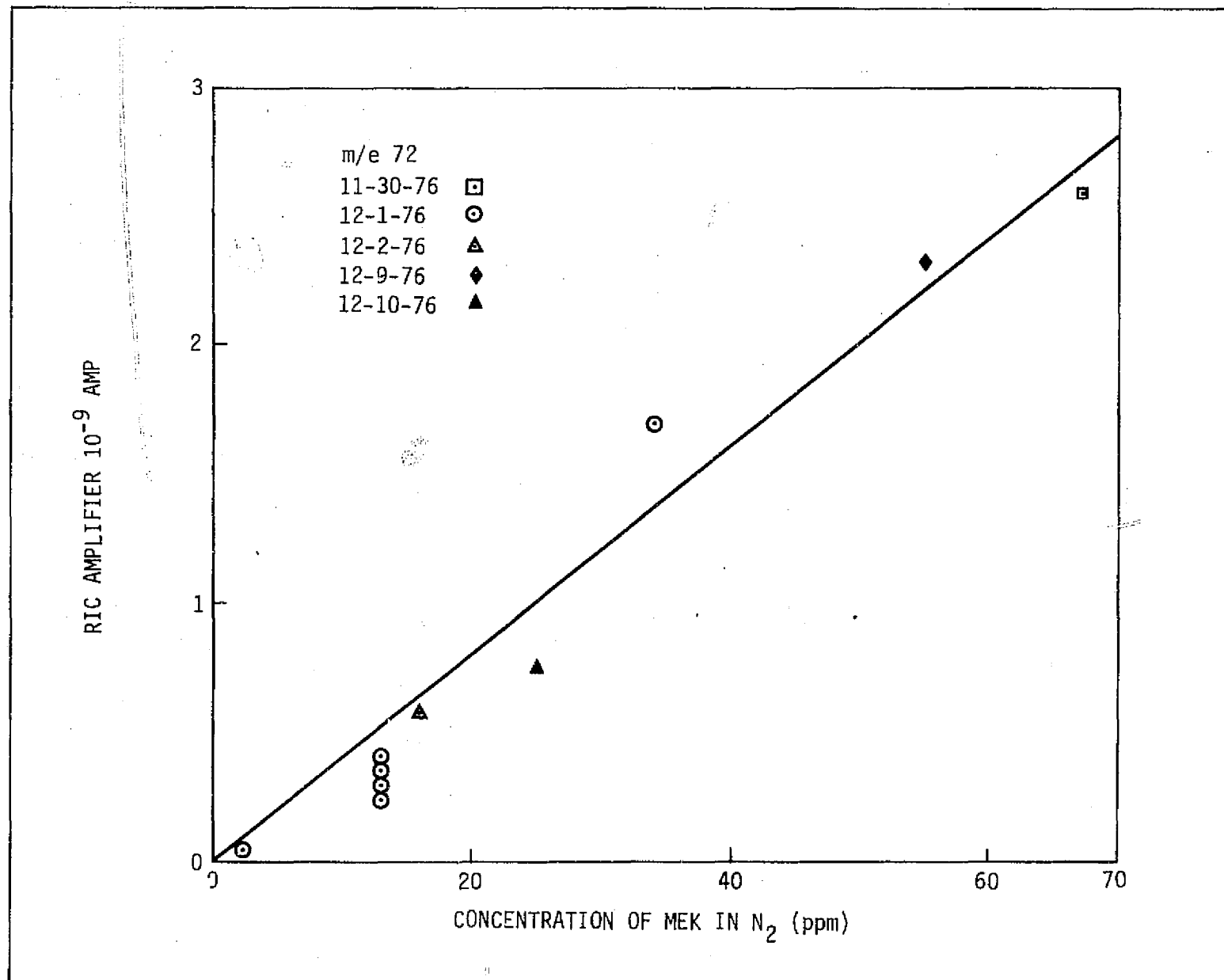


Figure 8-5. Calibration for Methyl Ethyl Ketone

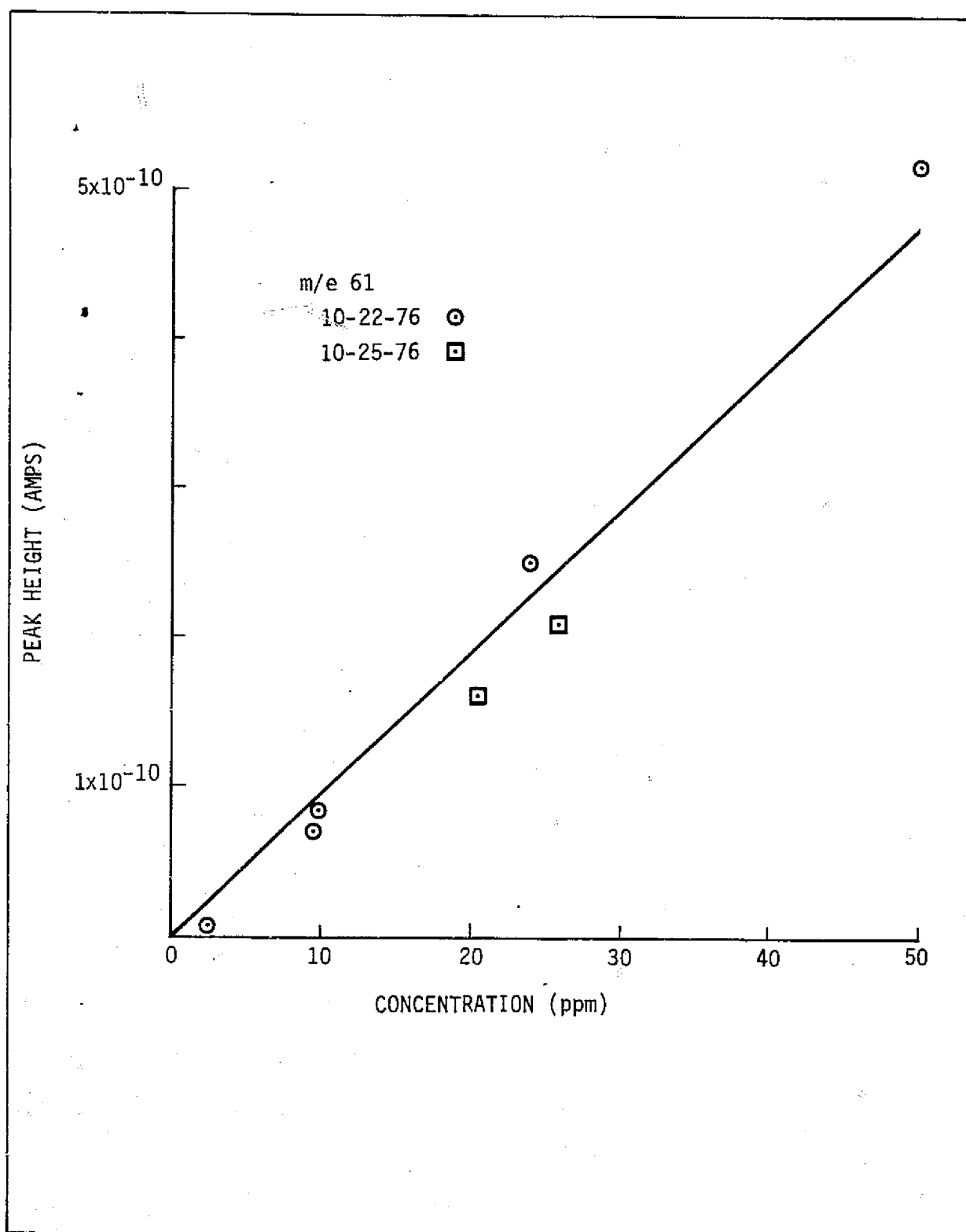


Figure 8-6. Calibration for Ethyl Acetate

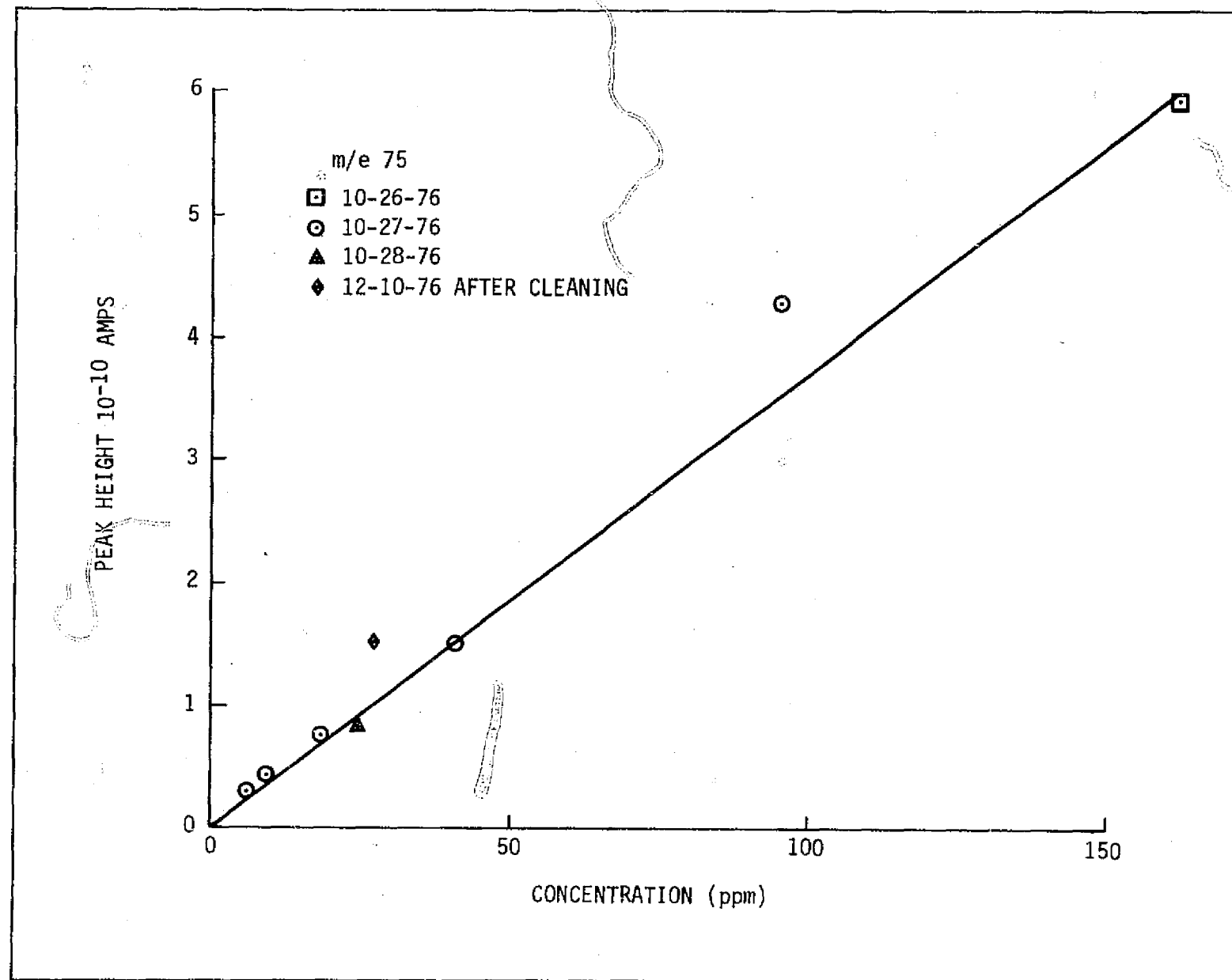


Figure 8-7. Calibration for Orthodichlorobenzene

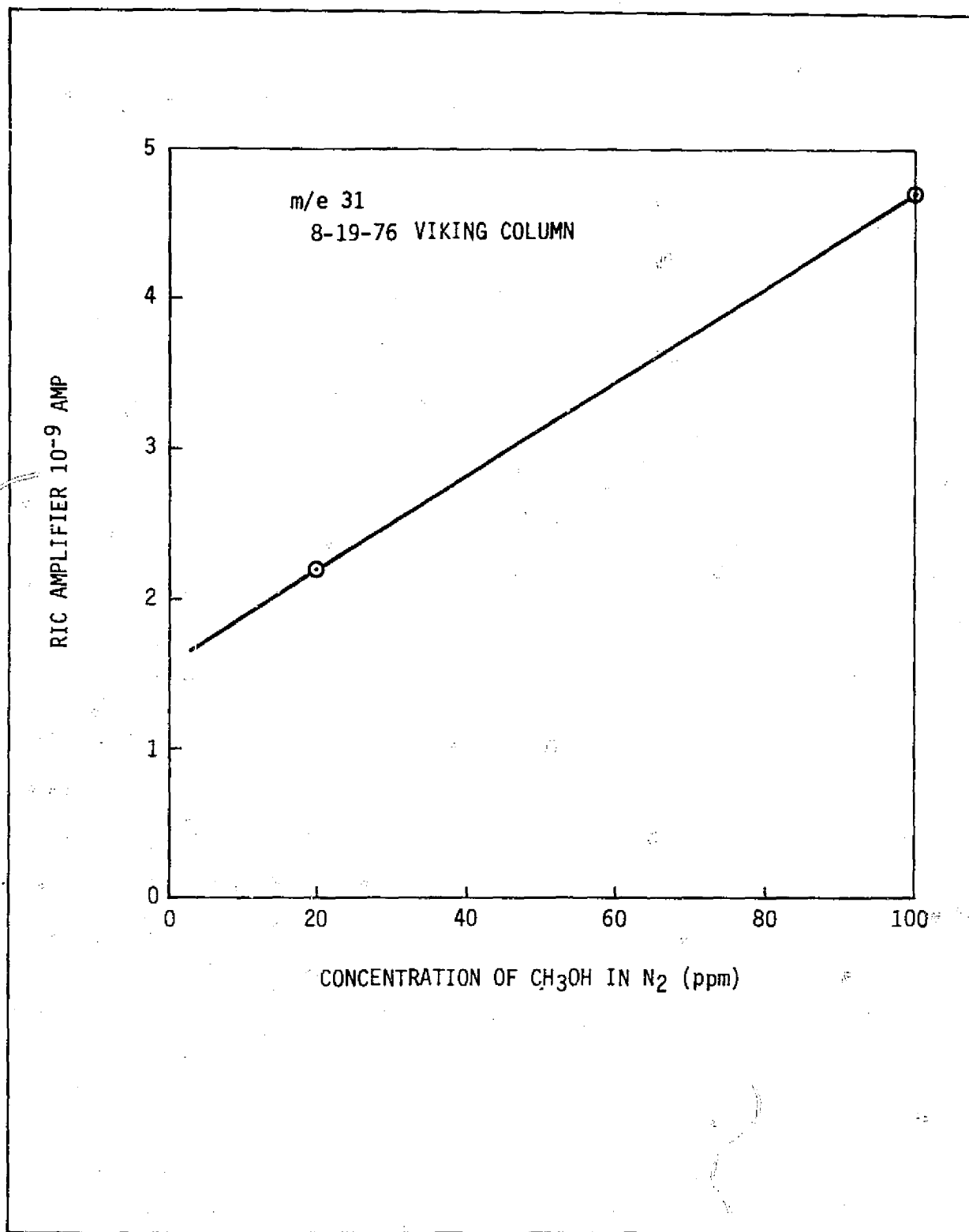


Figure 8-8. Calibration for Methyl Alcohol

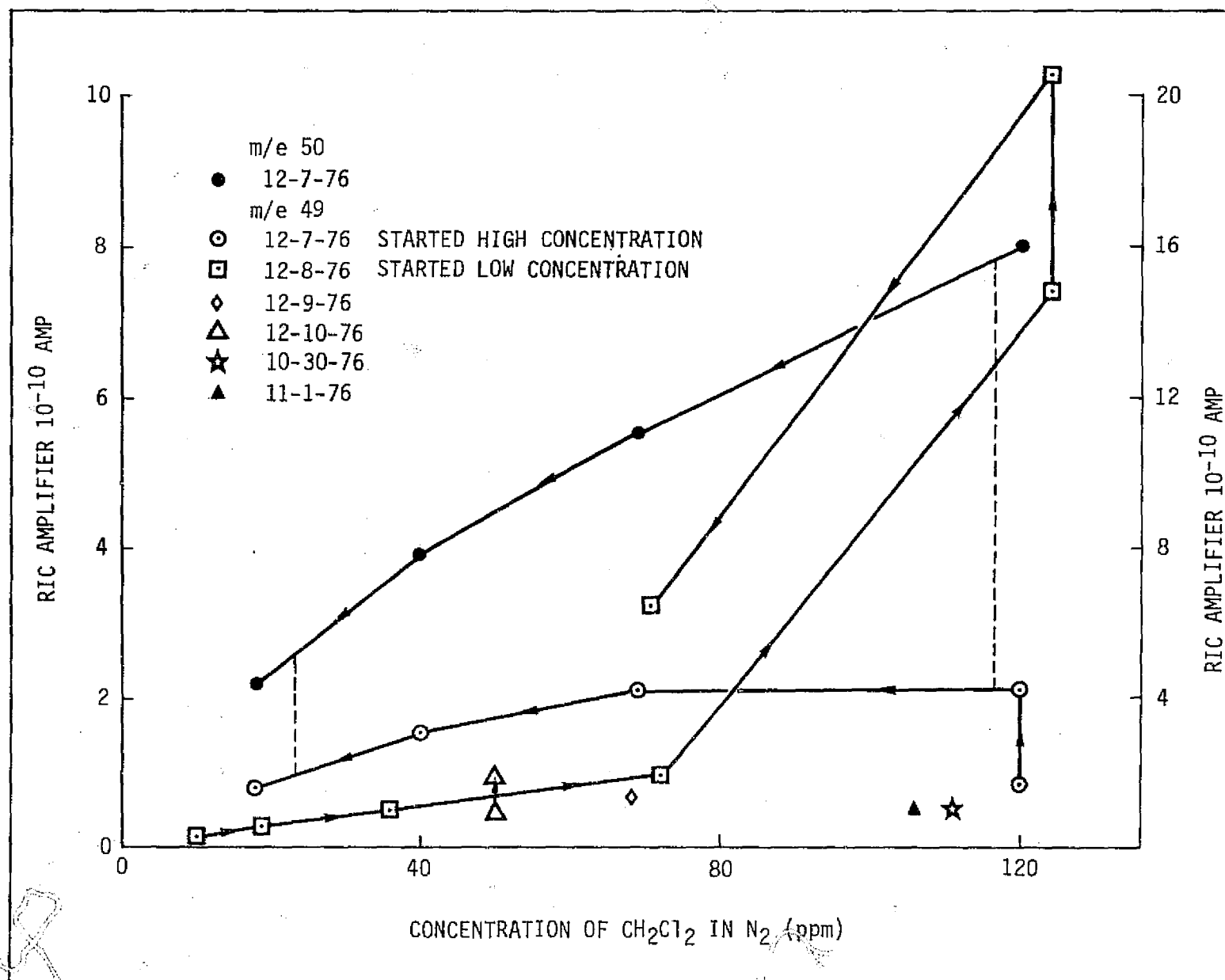


Figure 8-9. Calibration for Methylene Chloride

methyl alcohol, and carbon monoxide) produce linear curves that provide a means of estimating the approximate detectable limit (FIGURES 8-4 through 8-9). Because of the absence of a data system which would drastically decrease the amount of data produced, the calibration curves were made by single-ion monitoring of a characteristic ion from the compound that was injected. TABLE 8-5 shows the relationship of peak height to scan speed. From this table, it can be seen that the relationship of peak height versus scan speed depends not only on the scan speed but the peak height. As the peak gets more intense, the effect of scan speed is less. When a data system becomes available, the instrument will be calibrated at whatever scan speed is required for automatic operation. Peak height versus scan speed was also investigated by Perkin-Elmer during subsystem testing (Appendix III) and the same results were observed.

TABLE 8-6 is the summary of the test results on various compounds that were injected into the system. This table gives the concentration range of the samples injected and gives an approximate minimum detectable limit for each compound that was detected.

TABLE 8-5. SCAN SPEED VERSUS PEAK HEIGHT

28	Peak Height m/e		Scan Speed
	31	47	
3.2×10^{-9}	1.8×10^{-10}	2.4×10^{-11}	20 seconds/decade
3.0×10^{-9}	1.0×10^{-10}	0.65×10^{-11}	5 seconds/decade
2.3×10^{-9}	0.8×10^{-10}	0.6×10^{-11}	2 seconds/decade
1.1×10^{-9}	0.12×10^{-10}	0.3×10^{-11}	1 second/decade

During the testing on the various compounds, at least one complete mass scan was taken for each compound. From these scans it was noted that methylene chloride elutes as a mixture of methyl chloride and methylene chloride. It was also noted that dichlorobenzene elutes as benzene. A complete study of

TABLE 8-6. SUMMARY OF TEST RESULTS ON COMPLETE TGA BREADBOARD SYSTEM

Compound	Injected Sample Conc ppm	Sensitivity (Min Det Limit)		Mass Monitored	Comments
		Reqm't ppm	Perf ppm		
Methyl Ethyl Ketone	5 to 50	9.3	0.1	m/e 72	Linear response 5 to 50 ppm.
1-Butene	1000	250	No Data	m/e 56	No butene observed, probably elutes with air peak.
Ethyl Acetate	2 to 50	17.8	0.1	m/e 61	Linear response 2 to 50 ppm.
Methanol	20 to 100	2.8	2.0	m/e 31	Broad peak.
Carbon Monoxide	12 to 200	6.4	5.0	m/e 12	Linear response.
o-dichloro-benzene	6 to 160	2.3	0.2	m/e 75	Linear response 5 to 150 ppm, elutes as benzene.
Methylene Chloride	10 to 125	4.5	0.5	m/e 49	Random response 5 to 150 ppm.
Carbon Tetrachloride	50 to 100	0.9	See Comment	m/e 82	Data on these compounds are described under "Additional Tests," para 8.4.
Methyl Chloroform	60	0.85	See Comment	m/e 61	
Butyraldehyde	50 to 100	23.3	See Comment	m/e 72	Converts to butyric acid in system.

the various chlorinated compounds is included later in this report in paragraph 8.4.

It was observed that during continuation of testing, the effluent divider restrictors changed in restriction value. They appeared to increase their restriction value, possibly because of the polymerized butyraldehyde that was in the system. Contamination was evident when the slider valve was disassembled and white fuzzy material was observed on the tubing walls. Various solvents (acetone, alcohol, MEK, and Freons) were used to try to rinse contamination off the wall with little positive results. A solution of chromic acid was also used with some success rinsing off the contamination. After the tubing was cleaned and reassembled in the system, peak intensity of the various injected compounds (methyl ethyl ketone and ethyl acetate) was slightly larger. At present, the head pressure upstream of the effluent divider is somewhere between 25 and 30 psig. This pressure increase causes longer elution time for all the organic including the air. Higher pressure also spread the methanol peak. This was confirmed by running the effluent divider in the mode with V4, V5, and V6 opened, which lowers the system pressure.

Another requirement per the contract was to run precision sample analysis. The main concern was to get reproducibility results intradaily (the same day) and also interdaily (on different days). Considerable data were accumulated over the breadboard test phase under different operating conditions. The variation in operating conditions had considerable effect on the intradaily reproducibility of the injected samples.

Because the system was disassembled and cleaned during testing, causing the eluting peaks to have a larger amplitude, the interdaily tests showed a wider variation than would be normal for a system that was run under constant operating parameters. Problems with transmission of various chlorinated compounds through the hydrogen separator was discovered late in the test program. Considerable testing was done to determine which chlorinated compounds are affected by the separator and at what level this effect occurs. It can be noted that the reproducibility intradaily and interdaily of methylene chloride is very

inaccurate. This is due to the partial conversion of methylene chloride to methyl chloride in the separator. It appears from the data that there is some conditioning effect on silver palladium from repetition methylene chloride samples. All planned interdaily tests were not run but the ones that were characterized the reproducibility of the system. The intradaily reproducibility, in general, is better than 10%. The reproducibility data are summarized in TABLE 8-7.

The representative tests that were performed show that with minor modification the system operates as designed and will perform acceptably for a trace gas analyzer for space shuttle.

8.3.3 CO Testing

During initial CO testing, it was noted that the system background at mass 28 was very high and that low levels of CO could not be measured. Because of the fractionation of CO, a mass 12 peak results. It was decided to modify the system to monitor CO at mass 12. This was done by degaussing the magnet a minimum amount so that the instrument could scan down to mass 12. The consequence of degaussing the magnet was to lower the resolving power at high mass. Even though the resolving power was less, the instrument still meets the specification of a 10% valley at mass 200.

8.4 Additional Testing

Because of the problem encountered with chlorinated hydrocarbons, a separate set of tests was run to determine the effect a separator has on the chlorinated compounds. The system for these tests is shown in FIGURE 8-10. The various chlorinated compounds were injected first downstream of the separator in septum injector #2. The flow restrictor just upstream from the mass spectrometer limited the sample that entered the pumping system. The 0.5 ml volume during the test was either held at ambient temperature or raised to 260°C to determine the effect of hot stainless steel on the decomposition of the various chlorinated compounds. There was no apparent decomposition of the chlorinated compounds from being in contact with the hot stainless steel. A sample of

TABLE 8-7. REPRODUCIBILITY TESTS

Compound	Reproduction Interdaily Diff Days		Reproduction Intradaily Same Day		Comments
	Req	Tests No. CV*	Req	Tests No. CV*	
Methyl Ethyl Ketone	6	5 17%	6	6 11%	Apparently elutes with air.
1-Butene	6	None	6	None	
Ethyl Acetate	-	4 11%	-	2 2%	
Methanol	6	None	6	None	Eluted peak is very wide and has a long tail due to high column pressure.
Carbon Monoxide	6	4 18%	6	6 3%	Molecular Sieve column.
o-dichloro-benzene	6	4 30%	6	5 10%	Elutes from separator as benzene.
Methylene Chloride	-	5 70%	-	2 25%	There is some preconditioning effect.
Carbon Tetra-chloride	-	None	-	None	Will not transmit through the separator.
Methyl Chloroform	-	None	-	None	
Butyraldehyde	6	None	6	None	Material is converted to butyric acid in inlet system.

*CV is the coefficient of variation

butyraldehyde was also injected downstream in the separator and was found to decompose because of the hot stainless steel tubing. This sample mostly disappeared but some butyric acid was seen in the mass spectrometer. Each chlorinated sample was injected in septum injector #1 just upstream in the separator and the transmitted material was measured with the mass spectrometer. Two different separators were used during this chlorinated compound testing to see

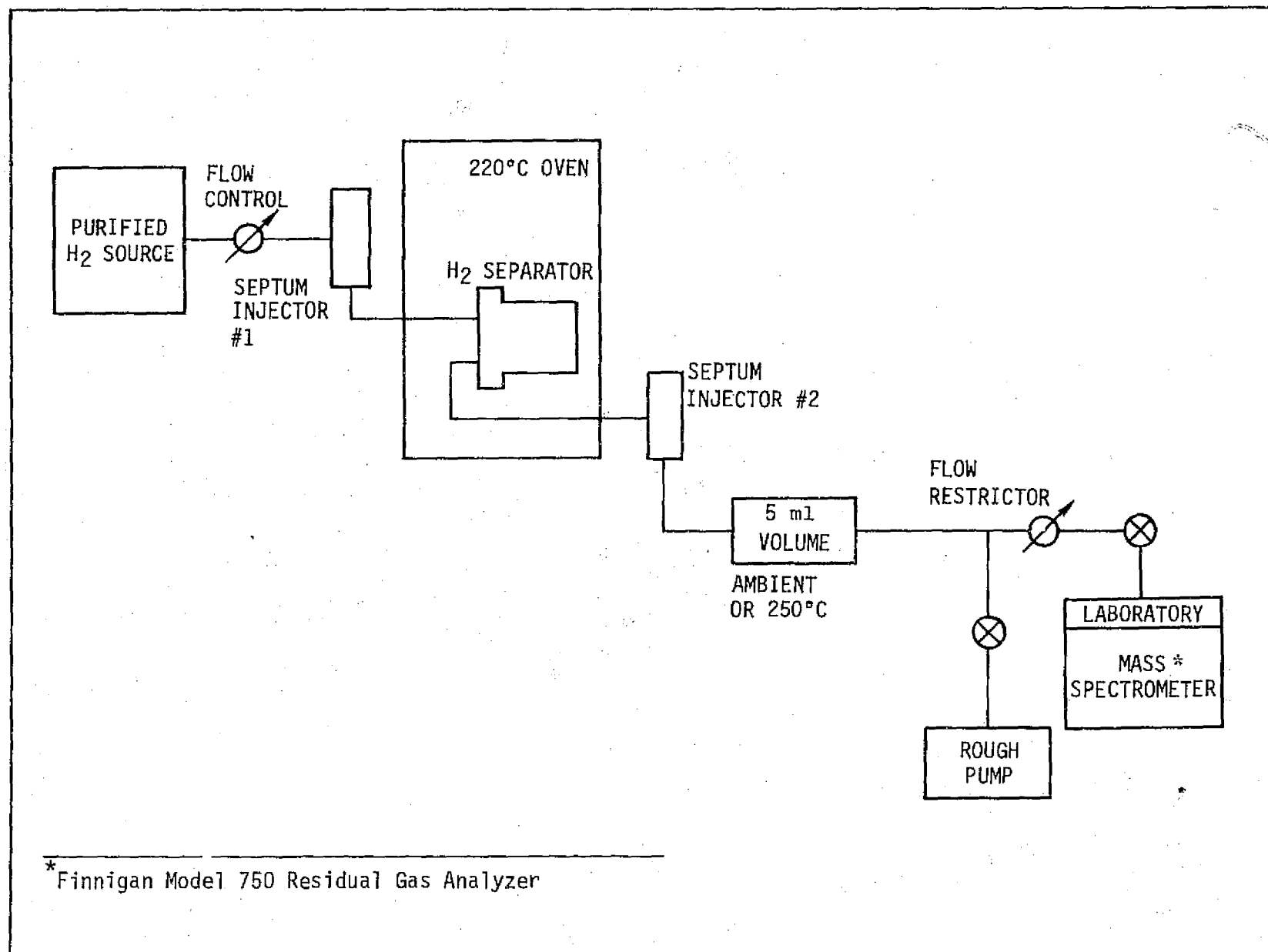


Figure 8-10. Block Diagram of Chlorinated Compound Test System

if lot material of the silver palladium had any effect on the decomposition. Both separators acted the same as far as partial transmission or decomposition of the various chlorinated compounds. Test results on the chlorinated compounds are summarized in TABLE 8-8.

A literature search (Appendix II) revealed that many chlorinated compounds do decompose when in contact with a good catalyst in a hydrogen atmosphere at relatively high temperatures (200°C). Even though platinum is used commercially as the catalyst, the silver palladium in our system is also a good catalyst and would most probably induce the same chemical conversion. This phenomenon of decomposition of chlorinated compounds was not observed on the Viking program because no chlorinated compounds were studied since they are not on the list of life-related compounds.

TABLE 8-8 (SHEET 1 OF 3). SUMMARY OF TEST RESULTS

Compound	Conc ppm	Column	System	Other Components	Result	Mass Scan ?	Conclusions
CH ₂ Cl ₂	100	GFE	TGA-BB	Complete BB with Slider Valve (SV)	CH ₂ Cl ₂ +CH ₃ Cl	Yes	No change was detected in an 1800 ppm sample of CH ₂ Cl ₂ passing through the separator. At 180 ppm it is about 50% con- verted to CH ₃ Cl and at 100 ppm down to less than 20 ppm it is about 75% converted to CH ₃ Cl.
	180	Viking	TGA-BB	Inject (No SV)	CH ₂ Cl ₂ +CH ₃ Cl	Yes	
	1800	Viking	TGA-BB	Inject (No SV)	CH ₂ Cl ₂	Yes	
	1800	None	Lab MS	H ₂ + Sep + Hot SS	CH ₂ Cl ₂		
	180	None	Lab MS	H ₂ + Sep + Hot SS	CH ₂ Cl ₂ +CH ₃ Cl	Yes	
CCl ₄	150	Viking	TGA-BB	Inject (No SV)	Many hydro- carbons (possible decomp of column)	Yes	When CCl ₄ is run through the Viking column many hy- drocarbons are shown in the MS. This probably in- dicates column degradation rather than a decomposition product of CCl ₄ .
	Large	Viking	TGA-BB	Inject (No SV)	Many hydro- carbons (possible decomp of column)	Yes	150 ppm CCl ₄ is unchanged by passing through a SS tube at 260°C. However, when a Sep is added, no detectable MS signal is obtained. Very large (~10% vapor) samples of CCl ₄ come through sep unchanged.
	100	GFE	TGA-BB	Complete BB w/SV			
	150	None	Lab MS	SS at 260°C, no Sep, w/wo H ₂			
	150	None	Lab MS	Sep + H ₂			

Note Abbreviations:

TGA-BB is Trace Gas Analyzer Breadboard
Lab MS is Finnigan Model 750 Mass Spectrometer

SS is stainless steel
Sep is electrochemical hydrogen separator

TABLE 8-8 (SHEET 2 OF 3). SUMMARY OF TEST RESULTS

Compound	Conc ppm	Column	System	Other Components	Result	Mass Scan ?	Conclusions
CCl ₄	Large	None	Lab MS	Sep + H ₂	CCl ₄	Yes	150 ppm CCl ₄ is unchanged by passing through a SS tube at 260°C. However, when a sep. is added, no detectable MS signal is obtained. Very large (~10% vapor) samples of CCl ₄ come
	150	None	Lab MS	Sep, No H ₂	Nothing	Yes	
CH ₃ CCl ₃	Large	Viking	TGA-BB	Inject	3 unidenti- fied peaks at mass 26 (possible decomp of column)	No	These results probably in- dicate column degradation by CH ₃ CCl ₃ . The Viking Column is not suitable for use with CH ₃ CCl ₃ .
	40	Viking	TGA-BB	Inject	Looks like hydrocarbons on mass scan	Yes	
	Large	None	Lab MS	Sep + H ₂	CH ₃ CCl ₃	Yes	CH ₃ CCl ₃ comes through the separator when its concen- tration is 200 ppm or greater. No compounds elute at 20 ppm.
	200	None	Lab MS	Sep + H ₂	CH ₃ CCl ₃	Yes	
	20	None	Lab MS	Sep + H ₂	Nothing	Yes	
	20	None	Lab MS	No Sep, w/wo H ₂	CH ₃ CCl ₃	Yes	
	20	GFE	TGA-BB	Complete BB Sep + SV	Nothing at Mass 61	No	

TABLE 8-8 (SHEET 3 OF 3). SUMMARY OF TEST RESULTS

Compound	Conc ppm	Column	System	Other Components	Result	Mass Scan ?	Conclusions
o-dichloro- benzene	2000	None	Lab MS	Sep + H ₂ , Inject	Benzene	Yes	o-dichlorobenzene is converted to benzene in the separator. By measuring m/e 75 a linear response was obtained from 5 to 150 ppm.
	300	None	Lab MS	No Sep	o-dichloro- benzene	Yes	
	5-150	GFE	TGA-BB	Complete BB	Linear response at m/e 75		
Butyral- dehyde	100	GFE	TGA-BB	Complete BB	Nothing at m/e 72	No	Butyraldehyde is converted to butyric acid in hot SS and is "lost" in the separator.
	250	None	Lab MS	Hot SS only	Butyric acid	Yes	
	250	None	Lab MS	Sep + H ₂	Nothing	Yes	

APPENDIX I

TGA SCIENTIFIC TEST PLAN FOR
TRACE GAS ANALYZER (TGA) PROGRAM

TGA SCIENTIFIC TEST PLAN
FOR
TRACE GAS ANALYZER (TGA) PROGRAM

Contract NAS9-14637

August 3, 1976

Prepared for:

National Aeronautics and Space Administration
Lyndon B. Johnson Space Center
Houston, Texas

Beckman*

INSTRUMENTS, INC.

ADVANCED TECHNOLOGY OPERATIONS
ANAHEIM, CALIFORNIA 92806

TGA SCIENTIFIC TEST PLAN

1.0 INTRODUCTION

The following is the Scientific Test Plan required by Section 3.3.4.2.1 of the Statement of Work for the Trace Gas Analyzer (TGA) (Phase II Breadboard, Contract NA39-14637).

The Scientific Test Plan is to be performed on an "All-Up" integrated system following successful completion of all engineering tests required by the Statement of Work.

2.0 ACCURACY AND PRECISION, INTRADAILY

Using the "All-Up" TGA Breadboard, six runs will be made on each compound. These six runs will all be made on each compound on the same day. For the samples which are liquid at ambient temperatures, these runs will be made on samples from permeation tubes (PT). The balance of the runs will be made on gas blend (GB) samples.

Compound

- Carbon Monoxide
- 1-Butene
- Methanol
- Butyraldehyde
- Methyl Ethyl Ketone
- O-Dichlorobenzene

3.0 PRECISION, INTERDAILY

Using the same samples and sources as listed under "Accuracy" in Section 2.0, five more samples of each compound will be run. No more than one sample of each compound will be run each day.

4.0 SYSTEM RESOLUTION, INTRADAILY

Using five permeation tubes all in the same oven and gas stream, the system resolution will be evaluated on six different days. The following compounds will be used in the test mixture.

- Methyl Ethyl Ketone
- Ethyl Acetate
- Methylene Chloride
- Carbon Tetrachloride
- Methyl Chloroform

(Note: The Viking Column may not resolve this mixture.)

5.0 SENSITIVITY LEVELS (MINIMUM DETECTABLE CONCENTRATION)

The minimum detectable concentration will be determined for each compound listed in Section 2.0 of this test plan. This will be done by running a sample in the vicinity of the required minimum detectable concentration then estimating the minimum detectable concentration to give $2/1 (S + N)/N$. The gas samples will be obtained by varying the gas flow rate over the permeation tubes.

APPENDIX II

LITERATURE SEARCH

LITERATURE SEARCH

A brief literature search was conducted in an effort to explain the behavior of the halogenated compounds in TGA.

Kozlik, et al¹ found that CCl_4 decomposes over catalytic surfaces at temperatures between 200° and 700°C to yield Cl_2 , C_2Cl_6 , C_2Cl_4 and C_6Cl_6 .

There was no evidence of this type of reaction occurring in the TGA system.

There is evidence in the literature² to show that CCl_4 is partially converted to HCCl_3 at 180°C over platinum. These conditions are similar to those encountered in the silver palladium separator which operates at 220°C .

Huntress³ reports that HCCl_3 continues to dehalogenate going to CH_2Cl_2 , CH_3Cl and CH_4 . When CH_2Cl_2 is run through the TGA system it is at least partially converted to CH_3Cl . We saw HCl when high levels of CCl_4 were run through a TGA separator, but no organic compounds were observed coming through the separator.

Busch and Stove⁴ showed that the following compounds are quantitatively dehalogenated over palladium-calcium carbonate catalyst at 20°C with one atmosphere of hydrogen:



This is consistent with our observation that o-dichlorobenzene is converted to benzene in the separator.

Polyphenyls can be synthesized⁵ by the action of hydrogen and a catalyst (palladium calcium carbonate) on dibromobenzenes. The reaction depends on the fact that the halogen is removed without being promptly replaced with hydrogen. Reactions of this type were not observed in TGA system test.

¹Kozlik, G.I., et al. *IZV, Vyssh. Uchebn. Zaved. Khim, Khim. Teknol*, 17(7) pp 1117-18 (1974).

²Mullin, C.R. and C.E. Wymore. U.S. Patent 3589596.

³Huntress "Organic Chlorine Compounds," Volume 3.

⁴Busch, M. and H. Stov. *Berichte*, 49 1063 (1916).

⁵Busch, M. and W. Weber. *J. Prakt. Chem.* 146 1 (1936).

APPENDIX III

CHARACTERIZATION TESTS ON
TGA MASS SPECTROMETER

Introduction

Mass spectra of selected compounds were obtained for the TGA analyzer to determine some of its performance characteristics. The compounds tested were nitrogen, carbon monoxide, carbon dioxide, methanol, butane, and carbon tetrachloride. Some data also was obtained for methane, perfluorobutane and perfluorokerosine. The primary purpose for these tests is to verify the instrument sensitivity for the trace gas analysis and to establish data that can be helpful in understanding the performance of the TGA GCMS system. In addition to the mass spectral data, therefore, some observations on the total ion current and the ion pump current are included.

Experimental

Samples of test gases were introduced to the mass spectrometer from a standard inlet system equipped with a Baratron capacitance manometer for pressure measurement. The system was maintained at 65°C; the capacitance manometer operated at 125°C for this inlet system temperature. The inlet system was connected to the mass spectrometer through a pin-hole leak in series with the 0.51 mm (0.020") diameter tubing. The conductance of the standard leak is 0.024 ml/s, and the conductance of the tubing is estimated at 0.048 ml/s. Effective conductance of this series leak is calculated to be 0.016 ml/s; using this value, the source sensitivity for nitrogen was shown to be consistent with earlier measurements obtained by a backfill technique. There are two shutoff valves in the leak line. One is a Nupro valve modified for low dead volume and equipped with a Vespel seat. The other was a standard Nupro 4H valve. The leak line was heated to approximately 150°C and the modified valve to 200°C. The pin hole leak and the flexible metal line that connected it to the inlet system were heated to 80°C. The system is shown schematically in Figure 1. The TGA mass spectrometer is operated at a source temperature of 220°C. Emission current is maintained at 400 μ A, and the electron multiplier gain is 4300 at 1800 V. Spectra were recorded on an oscillograph recorder with a 180-mm (7") chart span. Seven decades of signal level are available at 25.4 mm (one inch) per decade over the range from 10^{-6} - 10^{-11} A. The scale range from 10^{-11} to 10^{-12} A is 23 mm (0.9") and from 10^{-12} to 10^{-13} A is 13 mm (0.5"). The spectra presented in this report are obtained at a scan speed of 200 seconds/decade. Spectra were also recorded on 20, 5, and 2 seconds per decade to obtain data for comparison.

Experimental (cont'd)

Background spectra for the analyzer were usually recorded once a day. Spectra of the background in the inlet system were recorded several times during a series of spectral measurements. The nitrogen sensitivity was checked daily. Liquid samples were degassed by a freeze-pump-thaw cycle several times before introducing a sample.

ResultsMass Spectral Data

Mass spectral data are presented in Table 1. The numbers at the bottom of the column are the sensitivity in A/torr in the source (A/torr = 7.5 A/kPa). The source pressure is calculated using a conductance of 50 ml/s.

$$p_s = p_i \frac{C_e}{C_s}$$

The sensitivity relative to nitrogen is also reported. Nitrogen was the first gas tested and the data obtained indicated a source sensitivity of approximately 1.5×10^{-2} A/torr source. Butane was introduced next, and all subsequent nitrogen sensitivity measurements were approximately 30% lower, i.e., $S = 0.88 \times 10^{-2}$ A/torr. This effect is believed to be due to the effect of butane on the tungsten -3% rhenium filament. The signal output as a function of pressure is shown for the test gases in Figure 2-8. All of the test gases, except carbon tetrachloride and carbon dioxide, indicated a linear response over the pressure range tested. This maximum pressure tested was in the range from 13 to 63 MPa ($1-4 \times 10^{-5}$ torr) source. The non-linearity of carbon tetrachloride is not understood at present. The data for carbon dioxide is not sufficient to establish the nonlinearity conclusively. Errors in the mass spectra are those associated with noise on the ion currents at various mass numbers and inaccuracies in the pressure measurements. Noise is more significant for low pressure samples and for ions with low probability of occurrence, that is, small functional peaks. Inaccuracies in the pressure measurement are also more significant at low pressure. An estimate of the errors due to noise at different signal levels is presented in Table 2. These errors apply to data at slow (200 s/decade) scan speed. Generally in compiling the mass spectral data, the base peak was in the range from 5×10^{-9} to 10^{-7} A.

Table 2

<u>Signal Level</u>	<u>S/N pp</u>
10^{-7}	14.3
10^{-8}	4.3
10^{-9}	3.0
10^{-10}	1.0
10^{-11}	1.0
10	1.0

Results

Mass Spectral Data (cont'd)

Estimated Error in Ratio (%)
(2.5σ)

<u>Base Peak</u>	Ratio = 0.1	0.01	0.001
10 ⁻⁷	12	16	50
10 ⁻⁸	19	51	51
10 ⁻⁹	52	52	100

Reproducibility of the observed sensitivity values is estimated at 10% from the data obtained for nitrogen. Values for absolute sensitivity depend on the accuracy of the leak rate; the estimated uncertainty in this value is $\pm 20\%$.

The effect of scan speed on observed peak height is shown in Figures 10 in which the ion current for m/e 28 and m/e 14 of nitrogen are shown for four scan speeds. Attenuation for a signal of 10⁻⁹ is shown as a function of scan speed in Figure 10A. The attenuation is due to the increase of response time of the logarithmic electrometer at low signal levels.

Ion Pump Current

TGA ion pump current as a function of sample pressure was observed for certain compounds during the tests. Both the integral ion pump and the auxiliary ion pump were operated during these tests. The ratio of pump current for the TGA pump to the auxiliary pump was approximately 3. The data for the TGA pump are shown in Figure 10. The response of the TGA ion pump was slow for methanol. The source pressure stabilized (as indicated by the ion current at m/e 31) much more quickly than the ion pump current. It is believed that this is due to sorption of methanol in the instrument.

Pumpout Time

It is important for the operation of a GCMS that the transient gas sample is rapidly pumped from the source, so that spectra of subsequent GC peaks are not contaminated with earlier GC compounds. The pumpout time for methanol and carbon tetrachloride are shown in Figure 12. This data was obtained by closing the modified Nupro valve and cyclic scanning over the major peaks as the sample pressure decayed. The measurements therefore include the effect of the small line on the time constant. The data show that carbon tetrachloride pumps out much more rapidly than methanol and indicates that there will be significant tailing of polar compounds in the analyzer.

Total Ion Current

Total ion current is monitored by an electrode that intercepts part of the ion beam emerging from the ion source. The current measured is somewhat scan voltage dependent because the electrode is near the ion accelerating electrodes. It has been considered for use as a pressure transducer to normalize spectra obtained during GC operation. Total ion current at m/e 28 (scan voltage of ~1200V) are shown for four compounds in Figure 11. The ratio of total ion current at scan voltage of 1200 to that at 220 (m/e 150) is summarized in Table 3.

Table 3

Total Ion Current
Scan Voltage Dependence

<u>Sample</u>	<u>Ratio (TIC₂₈/TIC₁₅₀)</u>
Analyzer Background	2.0
Inlet System Background	2.6
Nitrogen	2.2
Carbon Tetrachloride	1.6

Mass Spectrometer Sensitivity

Capability of the mass spectrometer to meet the required detection level of 3×10^{-9} g/s at S/N = 3, is demonstrated by the measurements of methanol and carbon tetrachloride. A S/N_{pp} ratio = 3, is achieved at an output current level of 1×10^{-9} A. The flow of sample required to give 10^{-9} is for methanol at m/e 31 (from Figure 5).

$$\begin{aligned}
 Q_{\text{MeOH}} &= 1.45 \times 10^{-8} \text{ std ml/s} && (1.1 \times 10^{-5} \text{ torr cc/s}) \\
 &= \frac{1.45 \times 10^{-8} \text{ std ml/s (32 g/g-mole)}}{2.2 \times 10^4 \text{ std ml/g-mole}} && \left(\frac{1.1 \times 10^{-5} \text{ torr cc/s (32 g/g-mole)}}{1.7 \times 10^7 \text{ torr cc/g-mole}} \right) \\
 &&& (2 \times 10^{-11} \text{ g/s})
 \end{aligned}$$

for carbon tetrachloride at m/e 117 from Figure 8,

$$\begin{aligned}
 Q_{\text{CCl}_4} &= 9.2 \times 10^{-8} \text{ std ml/s} && (7.0 \times 10^{-5} \text{ torr cc/s}) \\
 &= \frac{9.2 \times 10^{-8} \text{ std ml/s (152 g/g-mole)}}{2.2 \times 10^4 \text{ std ml/g-mole}} && \left(\frac{7.0 \times 10^{-5} (152 \text{ g/g-mole})}{1.7 \times 10^7 \text{ torr cc/g-mole}} \right) \\
 &&& (6.2 \times 10^{-10} \text{ g/s})
 \end{aligned}$$

These calculations indicate that the mass spectrometer has more than adequate sensitivity for detection of chromatographic effluents at the required levels.

Resolution

Resolution at m/e 200 is determined with perfluorobutene-2 sample. The peak shape at m/e 200, 201 and 202 is shown in Figure 13. Since the peaks are not equal sized, it is necessary to estimate the percentage valley for equal size peaks. To do this, the peak separation is determined, and the ion current at a point corresponding to one half the peak separation is measured on either side of m/e 200. The percentage valley is the sum of these ion currents divided by the m/e 200 peak intensity. The resolution at m/e 200 is $M/\Delta M = 1$, at 5% valley.

MR/rjp

Table 1
Mass Spectra

<u>M/E</u>	<u>N₂</u>	<u>CO</u>	<u>CH₃OH</u>	<u>CO₂</u>	<u>Methane</u>
13		0.0004	0.035	0.0008	0.054
14	0.078	0.012	0.097	0.0014	0.11
14.5	0.0004				
15	0.0003		0.52		0.83
15.5			0.009		
16		0.004	0.003	0.13	1.000
22				0.021	
28	1.000	1.0	0.14	0.124	
29	0.0063	0.01	0.49	0.001	
30	0.0001	0.002	0.073	0.0003	
31			1.00		
32			0.71		
40	0.0018	0.0006		0.0007	
44				1.000	
45				0.011	
46				0.0036	
S(A/torr source)	8.8×10^{-3}	9.1×10^{-3}	4.4×10^{-3}	8.1×10^{-3}	
R	1	1.03	0.50	0.92	

Table 1 (cont'd)

Mass Spectra

<u>CCl₄</u>				<u>n Butane</u>			
<u>m/e</u>	<u>Relative Intensity</u>	<u>m/e</u>	<u>Relative Intensity</u>	<u>m/e</u>	<u>Relative Intensity</u>	<u>m/e</u>	<u>Relative Intensity</u>
13	0.006	50	0.0047	13	0.003	57	0.023
14	0.008			14	0.008	58	0.105
15	0.004	58.5	0.070	15	0.050	59	0.005
16	0.006	59.5	0.068				
17	0.014	60.5	0.022				
17.5	0.008	61.5	0.003	25	0.006	S(A/torr source) 8.9×10^{-3}	
18	0.18			26	0.063	R	1.0
				27	0.40		
		64	0.014	28	0.37		
20	0.063			29	0.53		
		70	0.018	30	0.012		
26	0.007	72	0.011				
27	0.011			37	0.008		
28	0.39	76	0.005	38	0.019		
29	0.007			39	0.10		
		82	0.33	40	0.02		
35	0.34	83	0.019	41	0.28		
36	0.11	84	0.21	42	0.12		
37	0.11	85	0.012	43	1.00		
38	0.035	86	0.036	44	0.03		
		87	0.002	45	0.003		
40	0.004						
41	0.013	117	1.000	50	0.012		
42	0.010	118	0.010	51	0.010		
43	0.004	119	0.95	52	0.002		
44	0.034	120	0.010	53	0.008		
		121	0.30	54	0.002		
47	0.043	122	0.004	55	0.010		
48	0.013	123	0.033	56	0.008		
49	0.14						

S(A/torr source) 1.1×10^{-3}

R 0.12

Table 1 (cont'd)
Perfluorobutene-2 Spectra

<u>m/e</u>		<u>m/e</u>	
31	0.47	131	1.000
43	0.19	132	0.036
50	0.051		
51	0.006	150	0.11
55	0.025	151	0.004
62	0.048		
69	0.95	162	0.007
70	0.009	163	0.008
75	0.14	164	0.002
81	0.045		
82	0.005	181	0.205
93	0.20	182	0.015
100	0.26		
101	0.005	200	0.133
112	0.059	201	0.005
113	0.505		

S 3.1 x 10⁻³

R 0.36

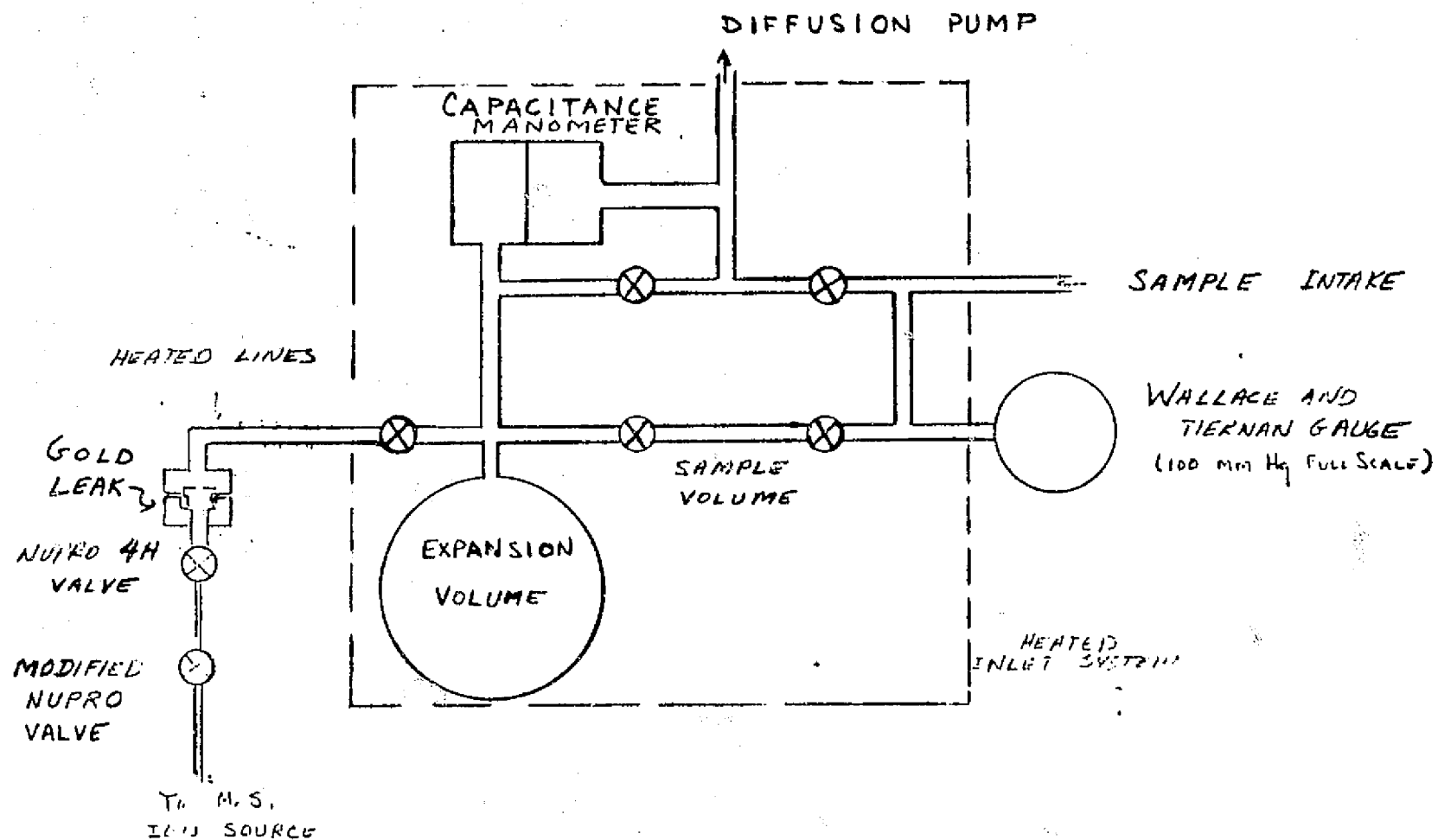


FIGURE 1.
INLET SYSTEM SCHEMATIC

46 7403

AMPS AT 15 MIN 28

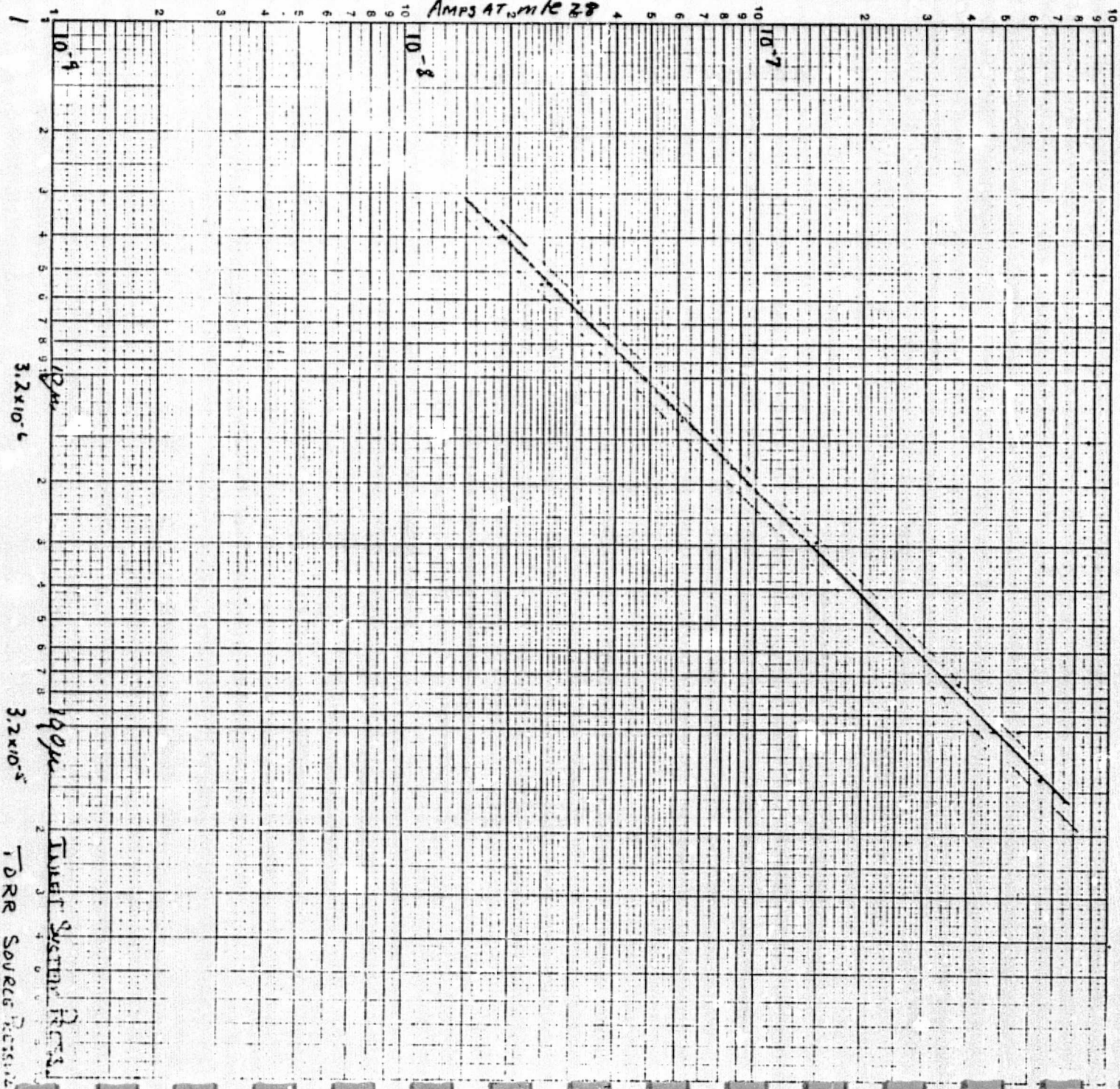
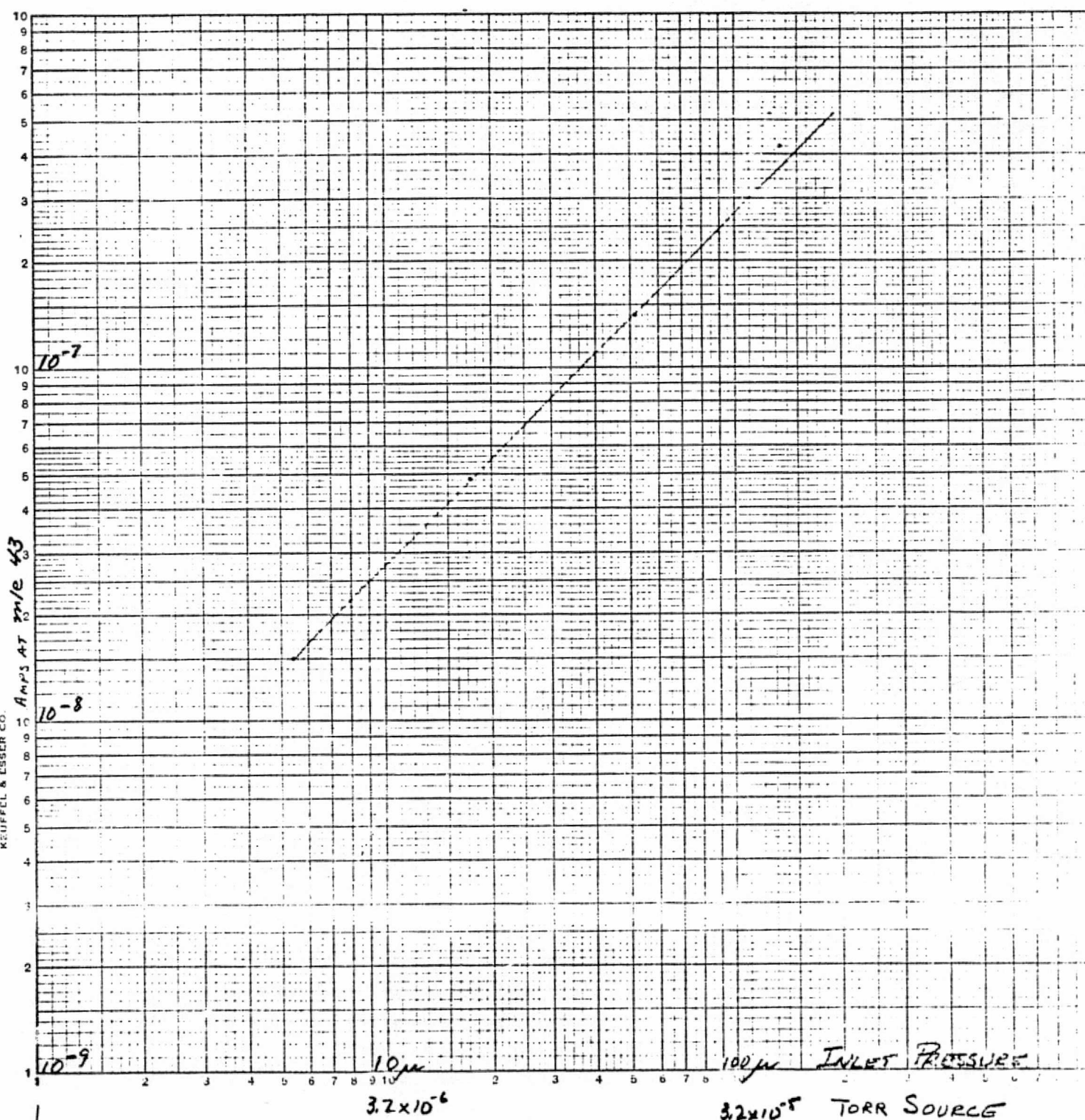
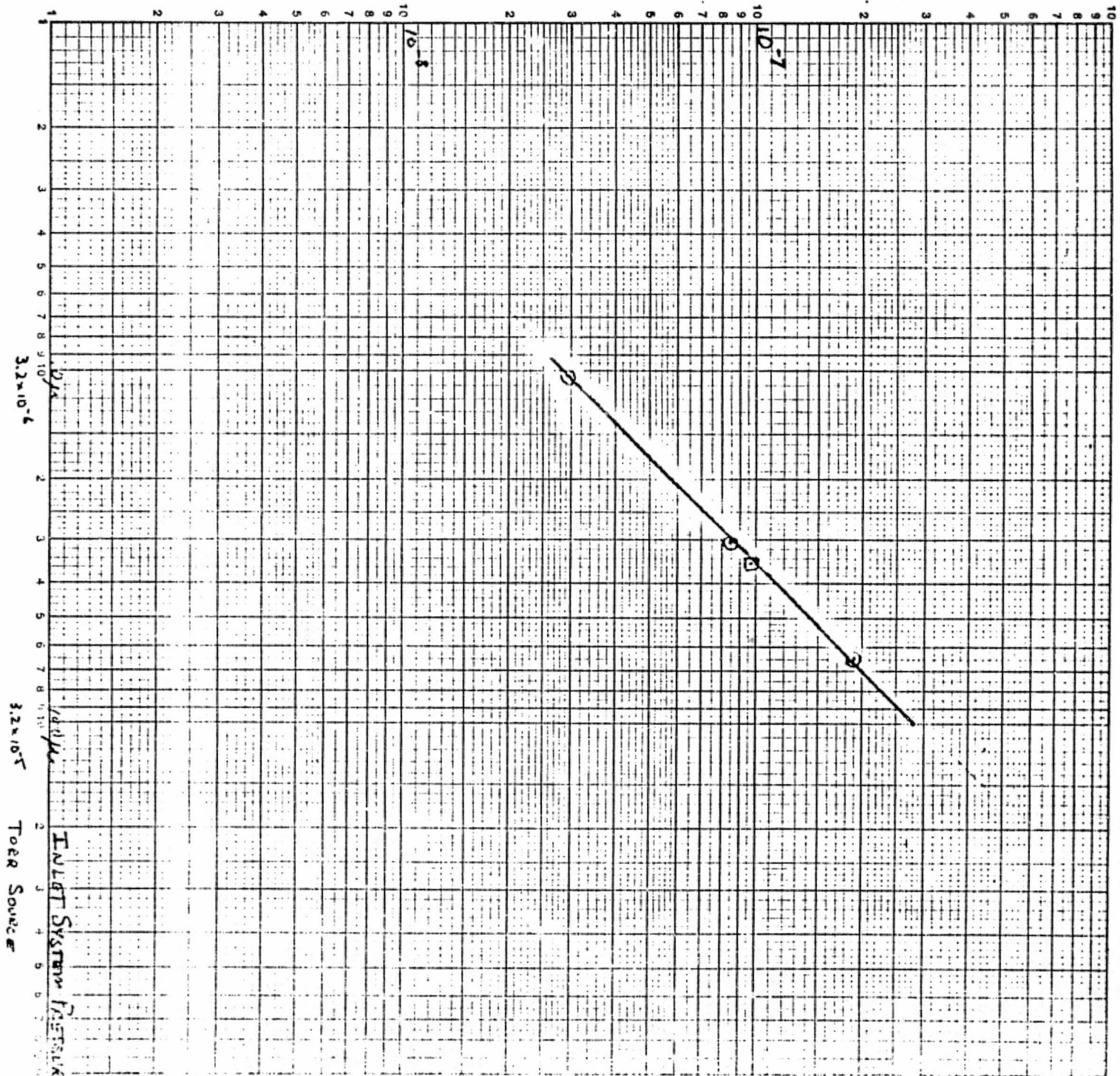


Fig. 3



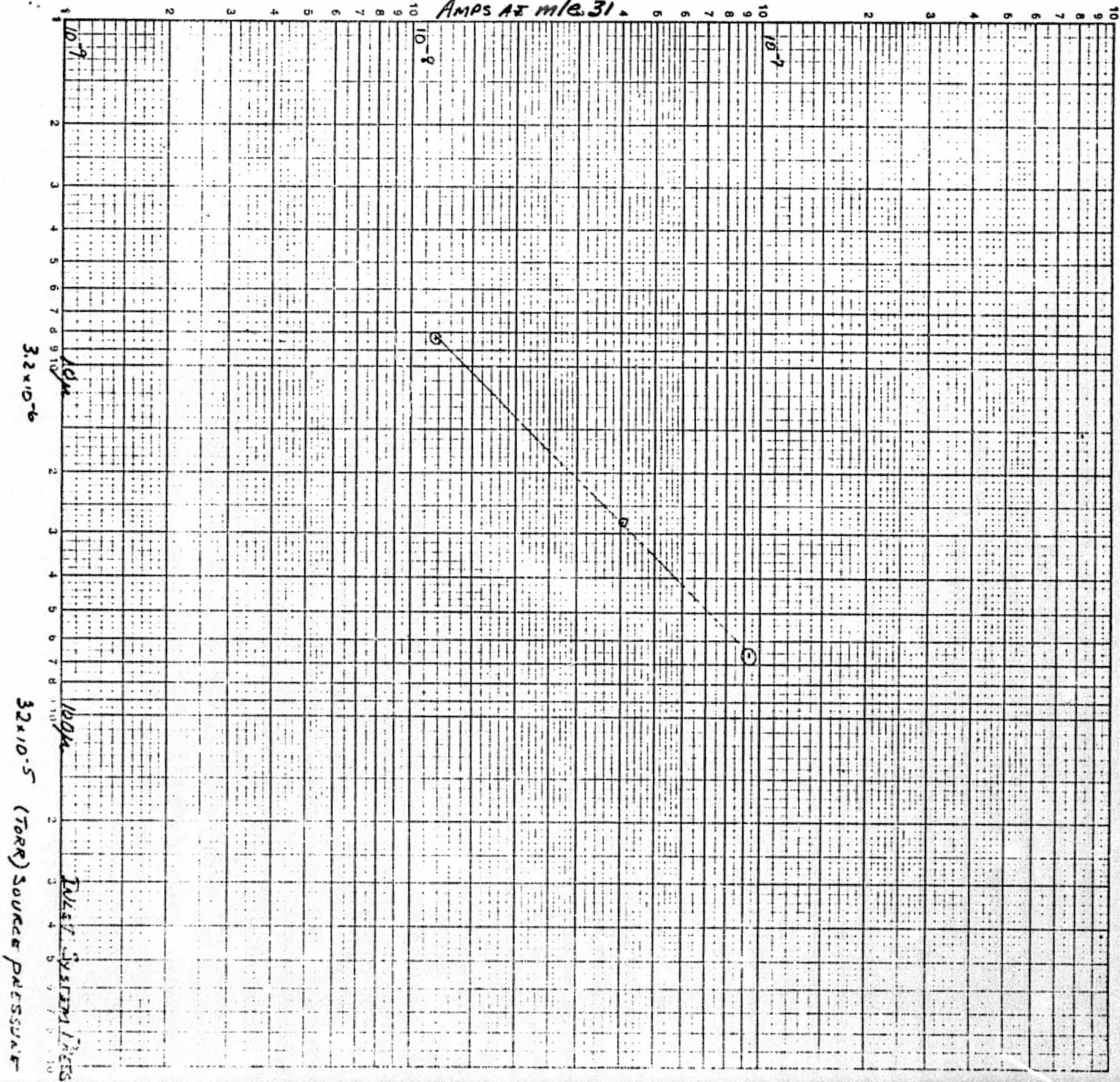
n-BUTANE PRESSURE

INLET PRESSURE
Torr SOURCE



NITROGEN AFTER FILAMENT EXPOSED TO BUTANE

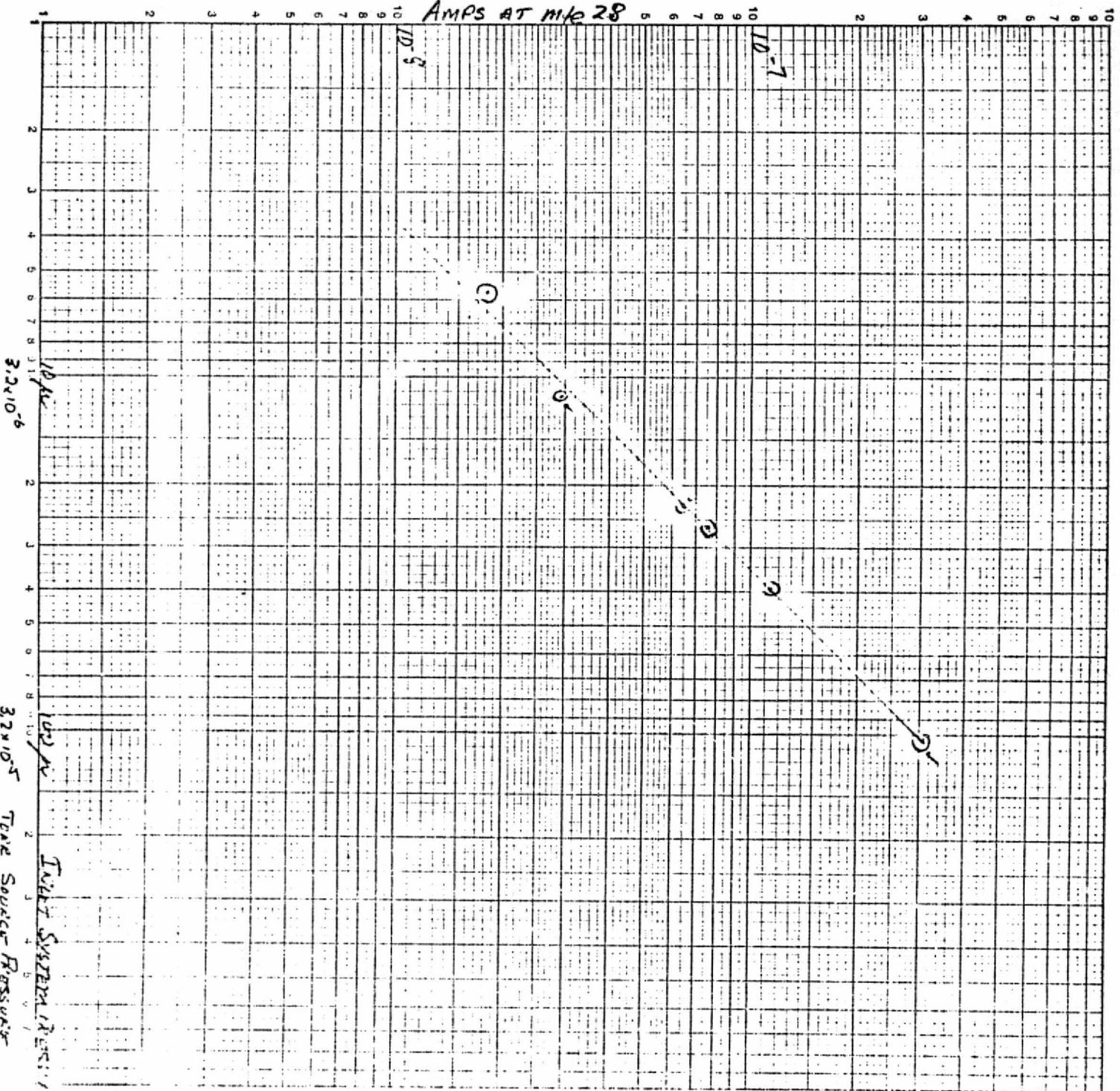
AMPS AT 112.31



METHANOL

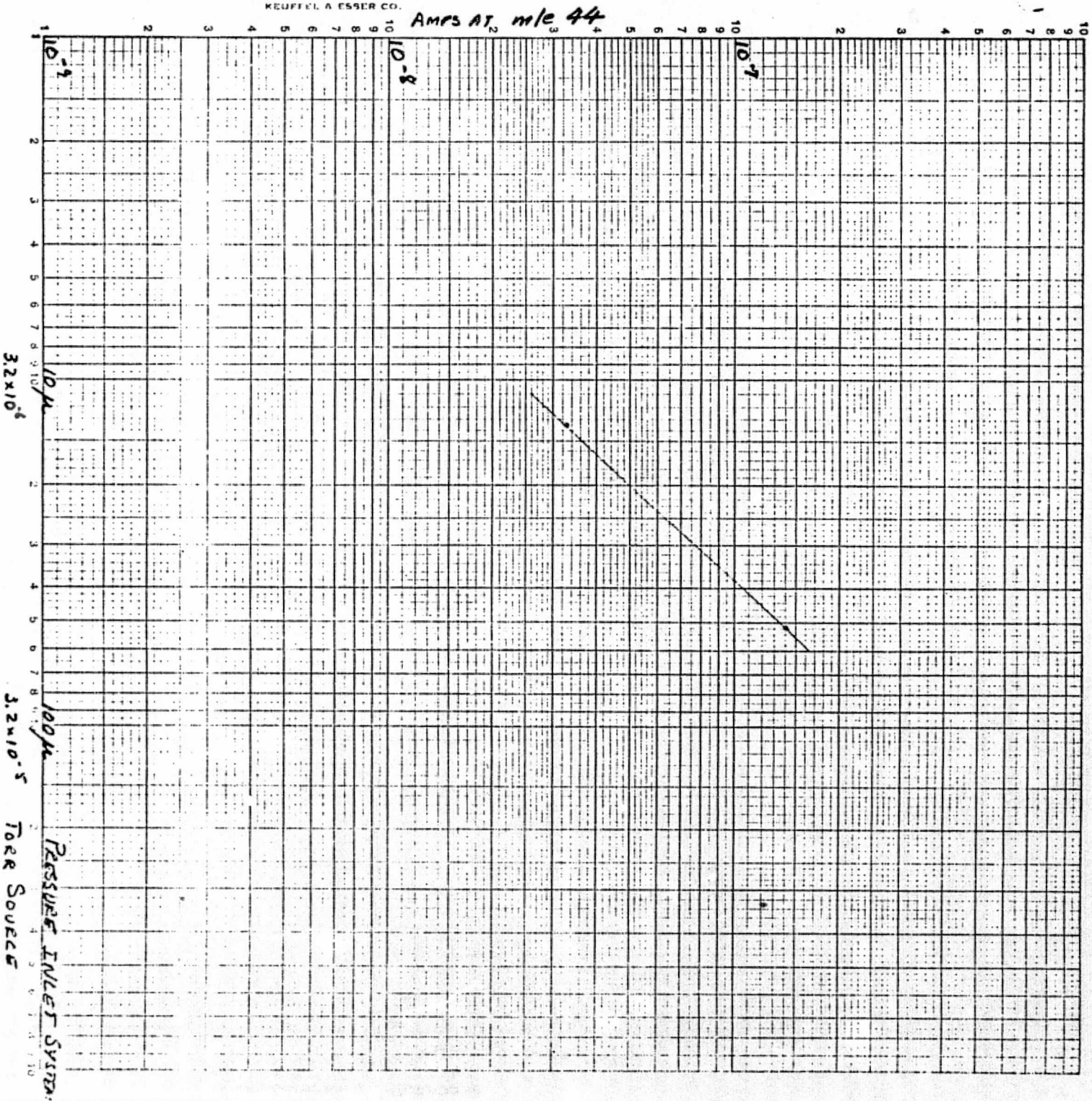
Figure 6

REPRODUCIBILITY OF THE
ORIGINAL PAGE IS POOR



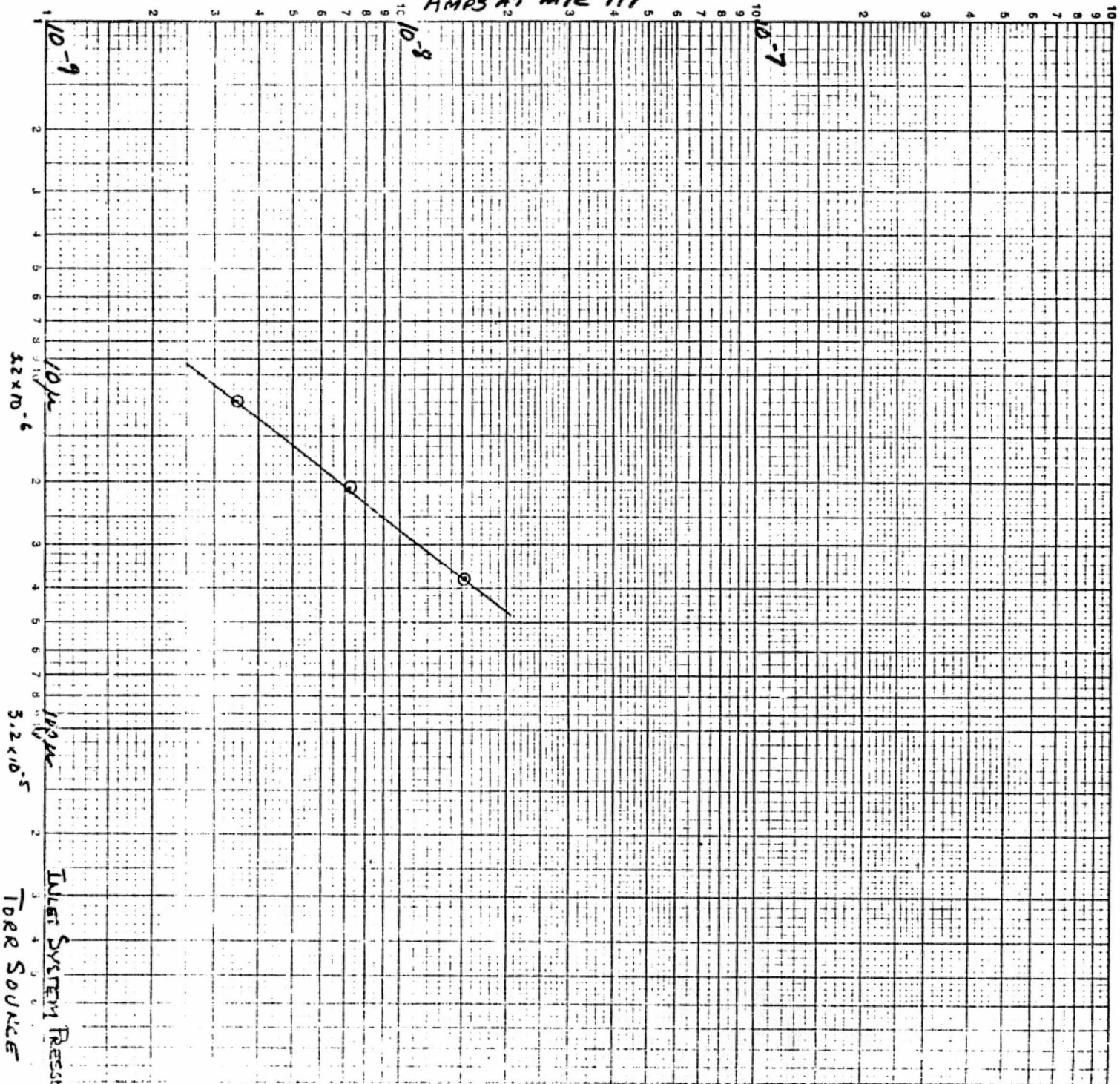
CARBON MONOXIDE

Figure 7



CARBON DIOXIDE

FIGURE 8.



CARBON TETRACHLORIDE

A-25

FIGURE 9
ION PUMP CURRENT

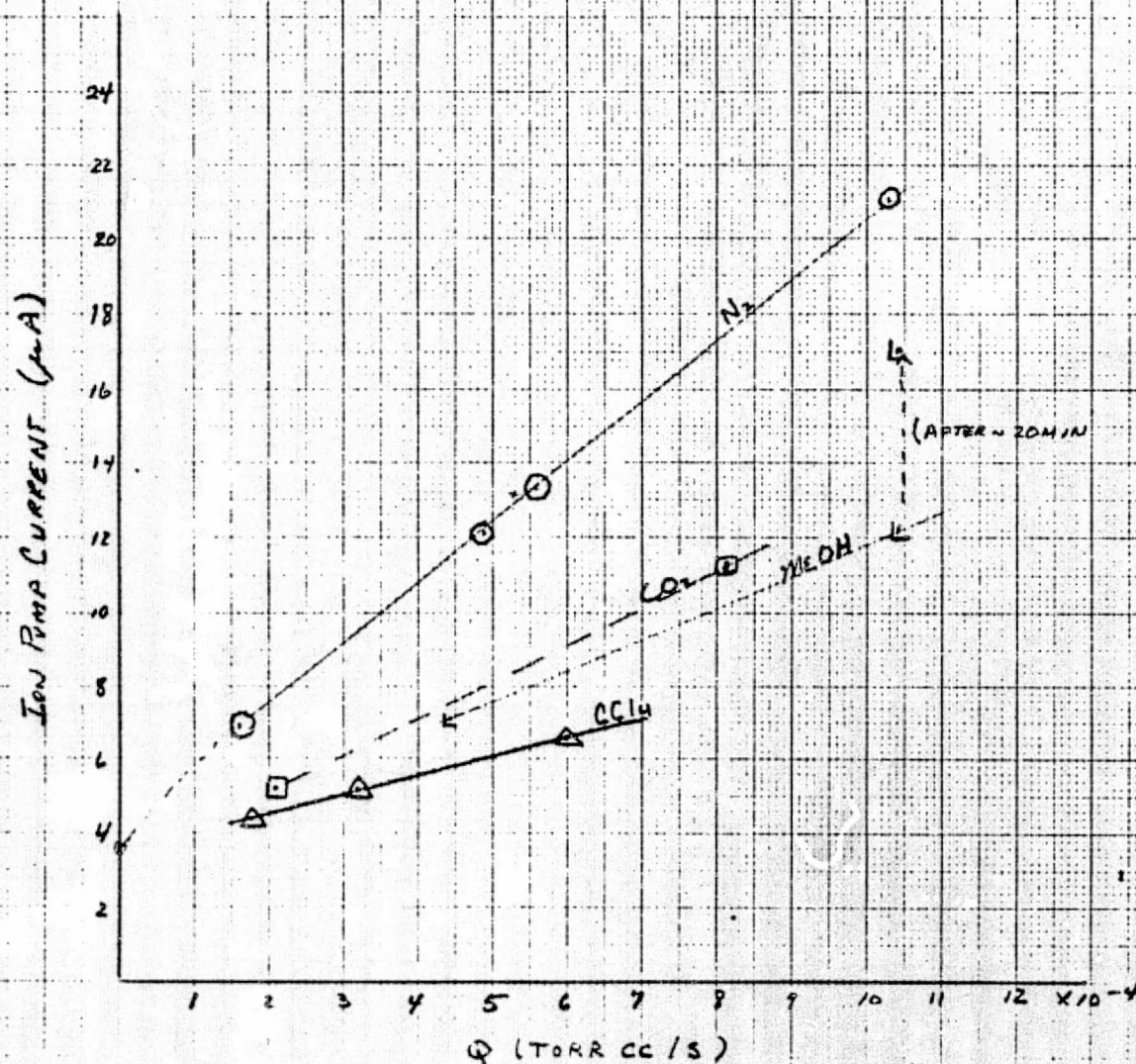
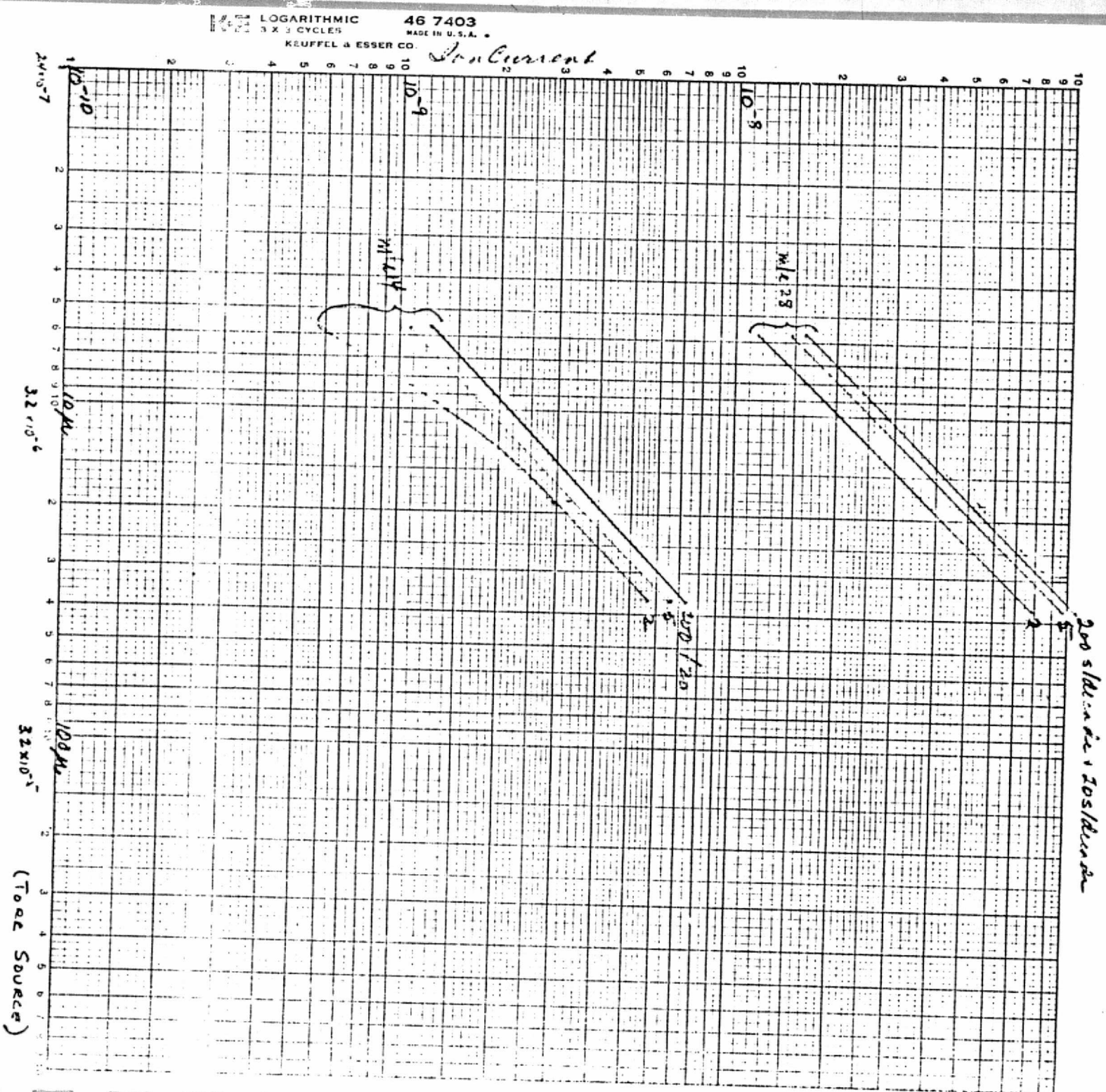


Figure 10



A-27

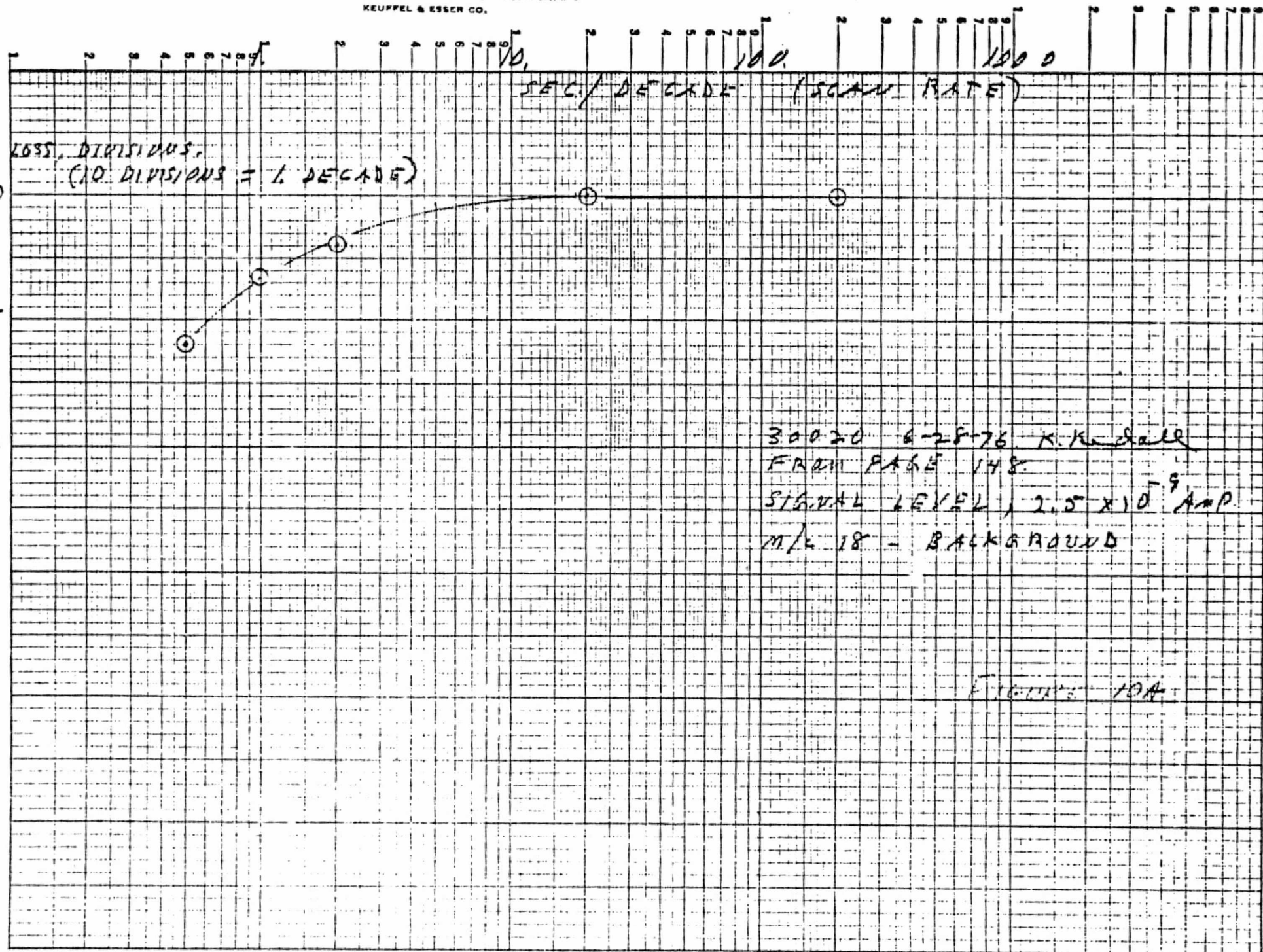
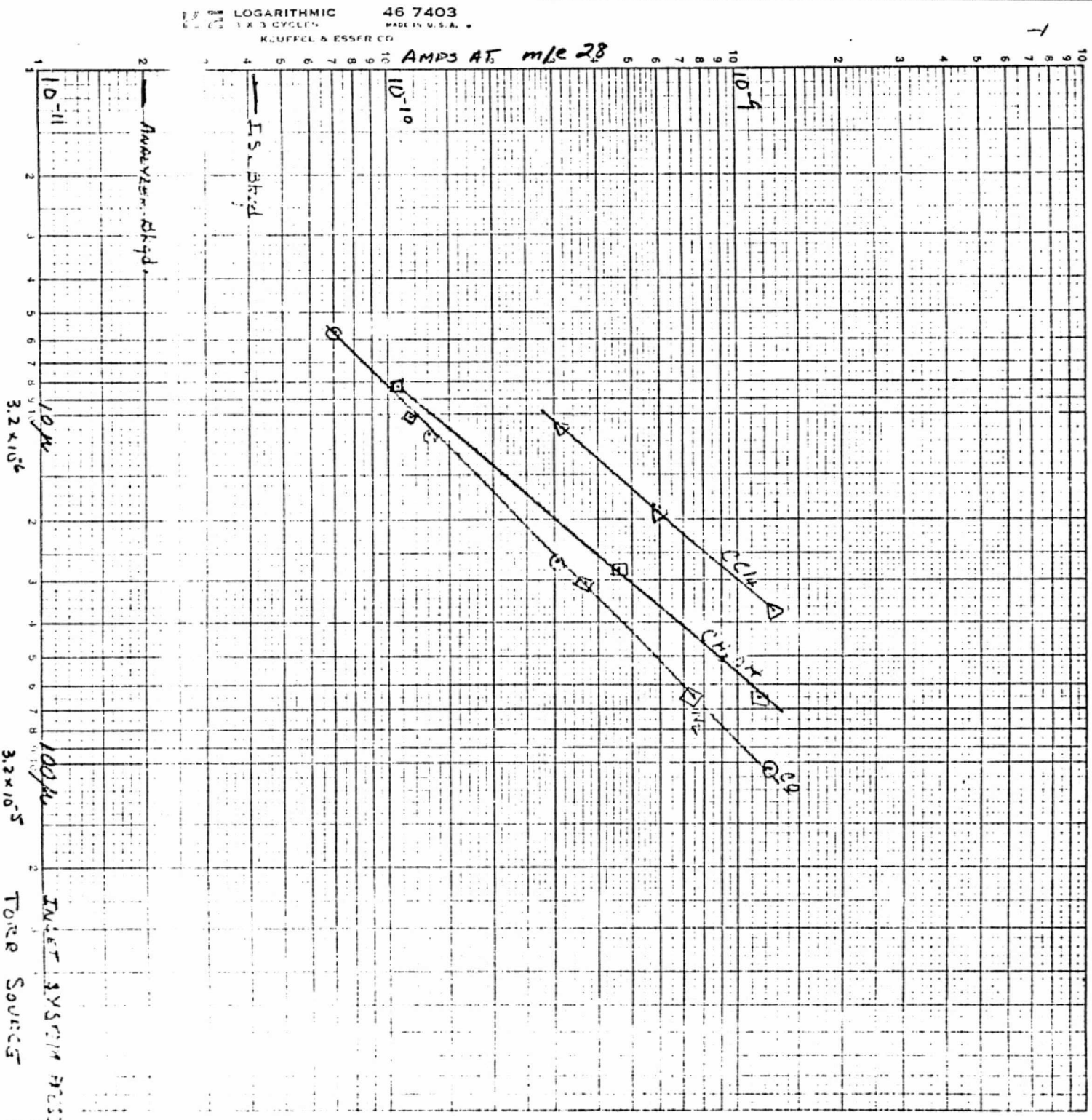


FIGURE 11



TOTAL ION CURRENT MONITOR

OUTPUT VARIATION WITH

SAMPLE PRESSURE

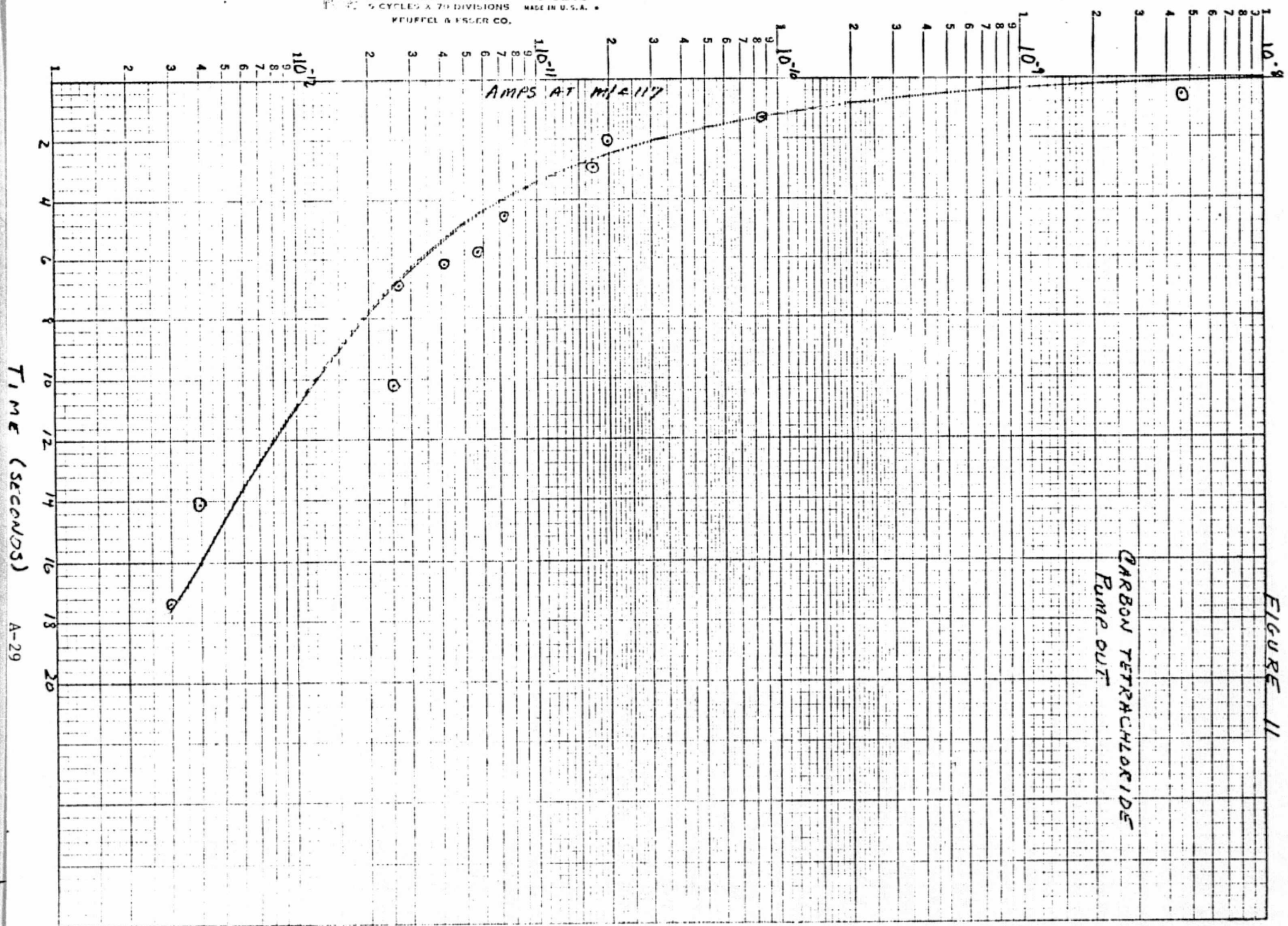


FIGURE 11

WATER (CONTINUOUS)

A-30

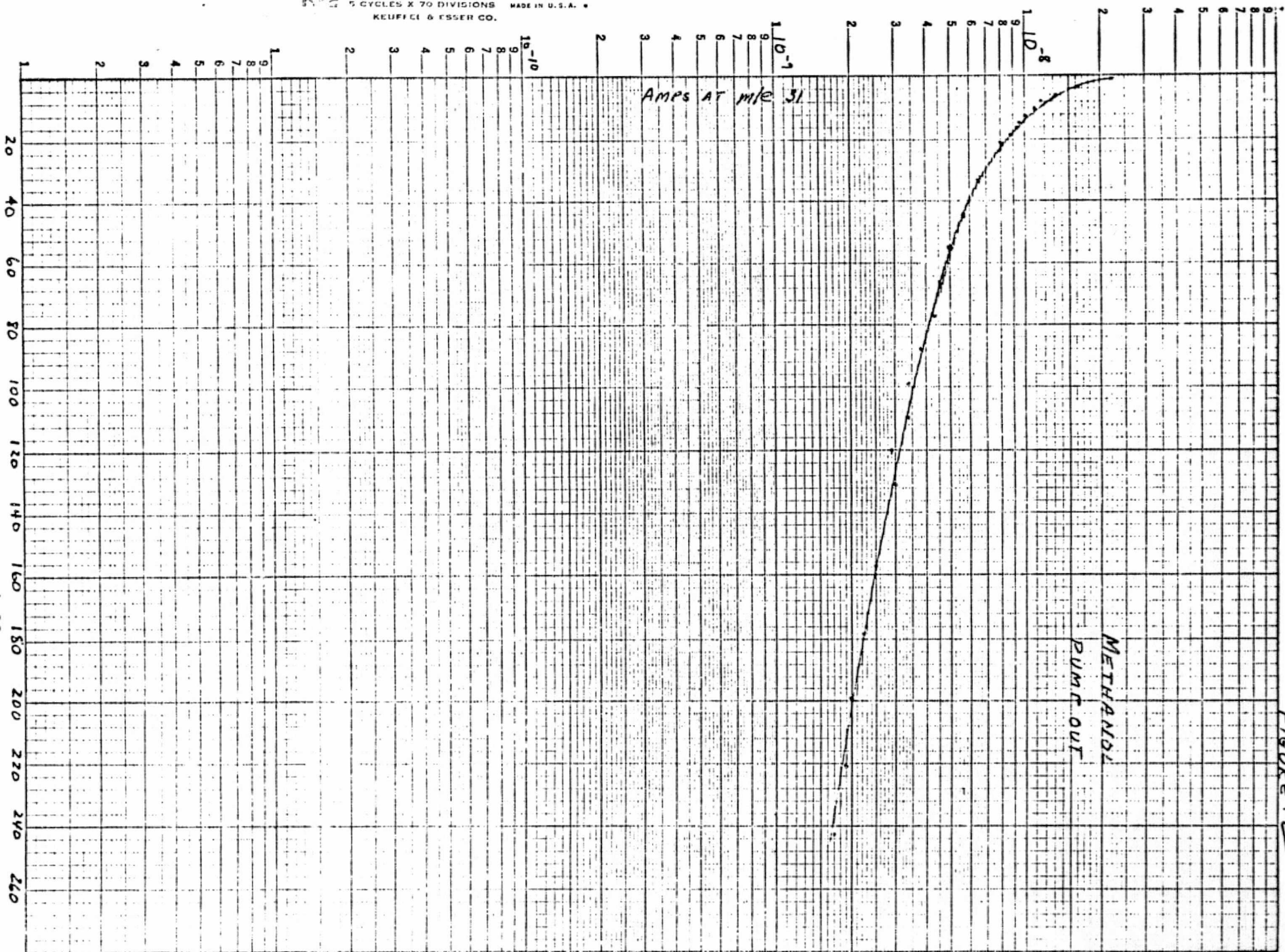


FIGURE 12

FIGURE 13
RESOLUTION

